

Mohammed A. Elmakki*, Orbett T. Alexander, Johan A. Venter and Andreas Roodt

The crystal structure of (carbonato κ^2O,O')(2-oxopyridin-1(2*H*)-olato- κN) tris(trimethylphosphine)rhodium(III) water solvate, $C_{15}H_{33}NO_5P_3Rh$

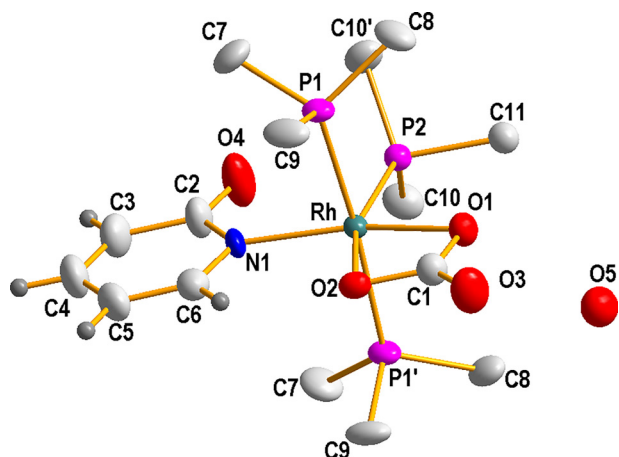


Table 1: Data collection and handling.

Crystal:	Yellow needle
Size:	0.24 × 0.05 × 0.04 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.03 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, ω
$\theta_{\max}$, completeness:	28.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26589, 2737, 0.068
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2249
$N(\text{param})_{\text{refined}}$:	150
Programs:	SHELX [1], Bruker [2], Diamond [3], Olex2 [4]

<https://doi.org/10.1515/ncrs-2022-0345>

Received July 5, 2022; accepted August 11, 2022;
published online September 12, 2022

Abstract

$C_{15}H_{33}NO_5P_3Rh$, orthorhombic, $Pnma$ (no. 62), $a = 19.8694(11)$ Å, $b = 12.5765(7)$ Å, $c = 8.6990(5)$ Å, $V = 2173.8(2)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0394$, $wR_{\text{ref}}(F^2) = 0.0941$, $T = 100$ K, $\alpha = \beta = \gamma = 90^\circ$.

CCDC No.: 2197355

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.

*Corresponding author: Mohammed A. Elmakki, Department of Chemistry, University of the Free State, 9301 Bloemfontein, South Africa, E-mail: azeez77777@gmail.com. <https://orcid.org/0000-0002-9084-3401>

Orbett T. Alexander, Johan A. Venter and Andreas Roodt, Department of Chemistry, University of the Free State, 9301 Bloemfontein, South Africa. <https://orcid.org/0000-0003-4926-8342> (O.T. Alexander)

Source of material

[Rh(opo)(CO)₂] (opo⁻ = 2-oxopyridin-1-olate) was synthesized according to the method described previously [5]. [Rh(opo)(CO)₃(P(CH₃)₃)] was synthesized by dissolving [Rh(opo)(CO)₂] (0.1000 g, 0.0495 mmol) in 5 cm³ of acetone under atmospheric conditions. Trimethylphosphine (P(CH₃)₃), in slight excess, was added to the prepared solution with stirring. Some ice water was added dropwise to precipitate the product. Upon water addition, a few yellow needle crystals formed from the acetone/water medium.

Experimental details

The methyl, aromatic and hydroxyl H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with fixed C–H distances for aromatic C–H of 0.93 Å (C–H) [$U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$], for methyl C–H of 0.96 Å (C–H) [$U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$]. The graphics were obtained using the DIAMOND [3] program with 50% probability ellipsoids. The highest peak is located 1.02 Å from P2 and the deepest hole is situated 0.74 Å from Rh1 respectively. Some hydrogen atoms in the figure are omitted for clarity.

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Rh1	0.37747 (2)	0.750000	0.73576 (4)	0.01974 (14)
P1	0.37592 (5)	0.56431 (7)	0.71743 (10)	0.0275 (2)
P2	0.38384 (6)	0.750000	0.99863 (13)	0.0232 (3)
O1	0.47939 (17)	0.750000	0.6872 (4)	0.0316 (8)
O2	0.40463 (18)	0.750000	0.5013 (4)	0.0258 (7)
O3	0.5143 (2)	0.750000	0.4409 (5)	0.0487 (11)
O4	0.2461 (2)	0.750000	0.9640 (5)	0.0583 (13)
N1	0.27323 (19)	0.750000	0.7112 (5)	0.0253 (9)
C1	0.4693 (3)	0.750000	0.5373 (6)	0.0307 (11)
C2	0.2270 (3)	0.750000	0.8272 (7)	0.0399 (13)
C3	0.1578 (3)	0.750000	0.7839 (8)	0.0478 (15)
H3	0.124276	0.750000	0.861671	0.057*
C4	0.1389 (3)	0.750000	0.6351 (8)	0.0494 (16)
H4	0.092447	0.750000	0.609052	0.059*
C5	0.1879 (3)	0.750000	0.5186 (7)	0.0437 (14)
H5	0.175334	0.750000	0.413208	0.052*
H11A	0.494 (2)	0.806 (4)	0.995 (5)	0.052*
H11B	0.482 (3)	0.750000	1.158 (8)	0.052*
H5A	0.1736 (19)	0.750000	1.095 (5)	0.052*
H5B	0.1034 (13)	0.750000	1.123 (6)	0.052*
C6	0.2533 (3)	0.750000	0.5604 (7)	0.0351 (12)
H6	0.286776	0.750000	0.482387	0.042*
C7	0.3008 (2)	0.4988 (3)	0.7879 (5)	0.0455 (10)
H7A	0.296297	0.511345	0.898588	0.068*
H7B	0.304071	0.422196	0.768522	0.068*
H7C	0.261242	0.527375	0.734588	0.068*
C8	0.4463 (2)	0.4933 (3)	0.7990 (5)	0.0418 (10)
H8A	0.488405	0.527787	0.767765	0.063*
H8B	0.445999	0.419677	0.762028	0.063*
H8C	0.442845	0.493862	0.911324	0.063*
C9	0.3781 (2)	0.5206 (3)	0.5185 (4)	0.0416 (10)
H9A	0.338962	0.549185	0.463760	0.062*
H9B	0.377004	0.442731	0.514819	0.062*
H9C	0.419442	0.546274	0.469661	0.062*
C10	0.3571 (2)	0.8606 (3)	1.1174 (4)	0.0394 (9)
H10A	0.376899	0.926568	1.078065	0.059*
H10B	0.372018	0.848951	1.223419	0.059*
H10C	0.307907	0.866033	1.114834	0.059*
C11	0.4734 (3)	0.750000	1.0402 (6)	0.0310 (11)
O5	0.1433 (2)	0.750000	1.1694 (5)	0.0446 (10)

Comment

There are several essential reactions with regard to homogeneous catalysis which transitional metal (preferably PGMs) complexes can undergo, such as oxidative addition, carbonyl insertion, substitution and reductive elimination. Oxidative addition is one type of reaction that can often be identified in the mechanistic scheme of catalytic processes. Understanding of catalytic processes requires fundamental research on homogeneous catalysis and relationships

between catalytic activity and the catalyst structure. One of the carbonyl ligands in the precursor [Rh(*L,L*-BID)(CO)₂] complexes (*L,L*-BID = different mono-charged bidentate ligands coordinated by e.g. O,O donor atoms such as cupferrate and 2-oxypyridin-1-olate, etc.) is substituted by tertiary phosphine ligands (PR₃) to form [Rh(*L,L*-BID)(CO)(PR₃)] complexes. These complexes have been studied intensively for potential applications in catalytic hydroformylation, hydrogenation, carbonylation, and decarbonylation. In this study the complex [Rh(opo)(CO)₃(P(CH₃)₃)] (opo[−] = 2-oxypyridin-1-olate) has been synthesized as part of a study to gain a better understanding of the electronic and steric influence of the phosphine ligands on the oxidative addition of methyl iodide [6–16]. Surprisingly, an atmospheric carbon dioxide molecule was captured by the rhodium complex, which was converted to a bidentate carbonato ligand in the aqueous solution.

In the title structure, the ligands are coordinated to rhodium in a distorted octahedral geometry around the Rh centre. The evident distortion is exhibited by the small bite angle of 63.269(2)° of the four membered chelate ring as well as the O1–Rh1–O2, N1–Rh1–P2, O2–Rh1–P1, N1–Rh1–P1, P1–Rh1–P2 and P1–Rh1–P1 angles of 63.269(2), 99.081(2), 86.409(1), 88.842(2), 93.954(1) and 171.018(1)°, respectively. Surprisingly, the opo[−] ligand is bonded monodentately *via* the nitrogen donor atom only, leaving the carbonato ligand as the sole bidentate coordinating entity in the structure. It is however mono-charged, since the oxygen O4 is deprotonated, balancing the charge to yield a neutral rhodium(III) species. Due to the less steric hindrance imposed by the trimethylphosphine ligands, the relative bond distance of Rh1–O1, Rh1–O2, Rh1–N1, Rh1–P1 and Rh1–P2; are 2.0684(1), 2.1104(1), 2.0824(1), 2.3411(1) and 2.2903(1) Å, respectively. There is a mirror plane which passes through the flat equatorial plane [N1–Rh–P1–O1–O2] of the structure and the trapped water solvent O5, resulting in only one half of the complex in the asymmetric unit, while the other half is symmetry generated.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: The authors acknowledge funding under the Swiss-South Africa joint research program (SSAJRP) from the SANRF (A. Roodt: UID: 107802) as well as from the Competitive Program for Rated Researchers of the SANRF (A. Roodt: UID: 111698), from the South African Department of Science Innovation (DSI) and the Department of Science and Technology (DST) respectively, “Department of Science and Innovation, Republic of South Africa” and “Department of Science and Technology, Republic of South Africa”.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

- Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
- Bruker. *SAINT-Plus (Version 7.12) and SADABS (Version 2004/1)*; Bruker AXS Inc.: Madison, WI, USA, 2004.
- Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. 3.0c*; Crystal Impact: Bonn, Germany, 2005.
- Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
- Elmakki M. A., Koen R., Venter J. A., Drost R. Crystal structure of dicarbonyl(pyridine-2-olate-1-oxido- κ^2O,O')rhodium(I), $C_7H_4NO_4Rh$. *Z. Kristallogr. N. Cryst. Struct.* 2016, *231*, 703–705.
- Roodt A., Visser H. G., Brink A. Structure/reactivity relationships and mechanism from X-ray data and spectroscopic kinetic analysis. *Crystallogr. Rev.* 2011, *17*, 241–280.
- Basson S. S., Leipoldt J. G., Roodt A., Venter J. A. Crystal structure of carbonyl(*N*-hydroxy-*N*-nitrosobenzenaminato-*O,O*tau)-triphenylphosphinerhodium(I). *Inorg. Chim. Acta* 1986, *118*, L45–L47.
- Basson S. S., Leipoldt J. G., Roodt A., Venter J. A. Mechanism for the oxidative addition of iodomethane to carbonyl(*N*-hydroxy-*N*-nitrosobenzenaminato-*O,O'*)-triarylphosphinerhodium(I) complexes and crystal structure of $[Rh(cupf)(CO)(CH_3)(I)(PPh_3)]$. *Inorg. Chim. Acta* 1987, *128*, 31–37.
- Uguagliati P., Deganello G., Belluco U. The system-dichlorotetracarbonyldirhodium-tertiary phosphines. *Inorg. Chim. Acta* 1974, *9*, 203–207.
- Brink A., Roodt A., Steyl G., Visser H. G. Steric vs. electronic anomaly observed from iodomethane oxidative addition to tertiary phosphine modified rhodium(I) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl $[PR_3 = PPh_3, PPh_2Cy, PPhCy_2, PCy_3]$. *Dalton Trans.* 2010, *39*, 5572–5578.
- Elmakki M. A., Koen R., Drost R. M., Alexander O. T., Venter G. J. S., Venter J. A. Crystal structure of carbonyl(2-oxopyridin-1(2*H*)-olato- κ^2O,O')(triphenylphosphine- κP)rhodium(I), $C_{24}H_{19}NO_3PRh$. *Z. Kristallogr. N. Cryst. Struct.* 2016, *231*, 781–783.
- Elmakki M. A., Alexander O. T., Venter G. J. S., Venter J. A. Crystal structure of carbonyl(2-oxopyridin-1(2*H*)-olato- κ^2O,O')(diphenylcyclohexylphosphine- κP)rhodium(I), $C_{24}H_{25}NO_3PRh$. *Z. Kristallogr. N. Cryst. Struct.* 2017, *232*, 831–833.
- Elmakki M. A., Alexander O. T., Roodt A. The crystal structure of trans-carbonyl-(diphenylcyclohexyl-phosphine- κP)iodidomethyl-(2-oxopyridin-1(2*H*)-olato- κ^2O,O')rhodium(III), $C_{25}H_{28}INO_3PRh$. *Z. Kristallogr. N. Cryst. Struct.* 2020, *235*, 279–281.
- Elmakki M. A., Alexander O. T., Venter J. A., Roodt A. Crystal structure of carbonyl(2-oxopyridin-1(2*H*)-olato- κ^2O,O')(triphenylarsine- κAs)rhodium(I), $C_{24}H_{19}AsNO_3Rh$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 223–225.
- Elmakki M. A., Alexander O. T., Venter J. A., Roodt A. Crystal structure of carbonyl(2-methylquinolin-8-olato- κ^2N,O)(triphenylarsine- κAs)rhodium(I), $C_{29}H_{23}AsNO_2Rh$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 215–217.
- Elmakki M. A. E., Alexander O. T., Venter G. J. S., Venter J. A., Roodt A. Synthesis and structural determination of $[Rh(opo)(CO)(PR_3)]$ complexes (*opo* = 2-oxopyridin-1-olate) and in situ isomeric behavior from preliminary kinetic study of iodomethane oxidative addition. *J. Coord. Chem.* 2021, *74*, 444–466.