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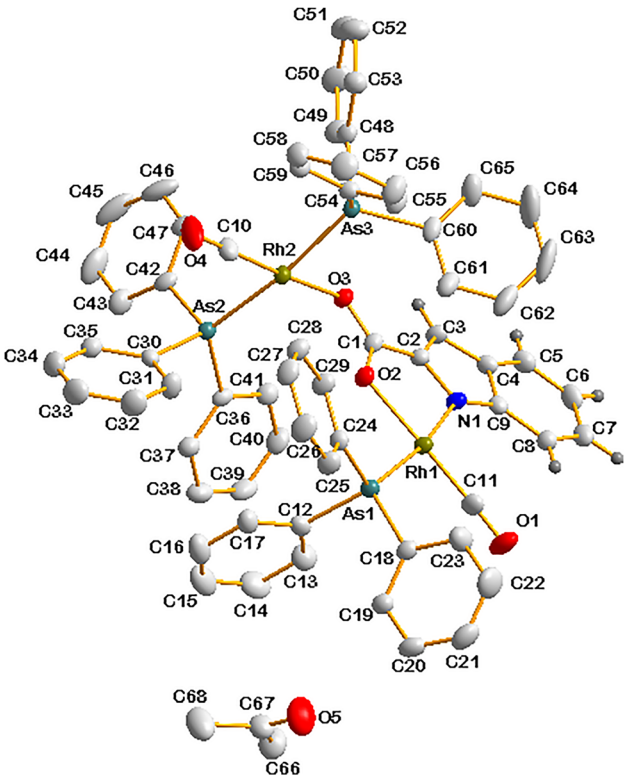
Crystal structure of dicarbonyl (μ_2-indole-2-carboxylato κ^2*O:O′*)tris(triphenylarsine-*κAs*) dirhodium(I) acetone solvate, $C_{68}H_{56}As_3NO_5Rh_2$



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Abstract

$C_{68}H_{56}As_3NO_5Rh_2$, triclinic, $P\bar{1}$ (no. 2), a = 14.048(4) Å, b = 14.569(4) Å, c = 17.942(5) Å, α = 92.273(9)°, β = 112.728(9)°, γ = 115.910(9)°, V = 2948.7(13) Å^3, Z = 2, $R_{gt}(F)$ = 0.0378, $wR_{ref}(F^2)$ = 0.0990, T = 100 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.

1 Source of materials

The 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-chloro-tetracarbonyldirhodium(I), $[RhCl(CO)_2]_2$.[5–7] The addition of an equivalent amount of indol-2-carboxylic acid (indol(H_2)) to the aforementioned yellow solution followed by addition of ice water yielded the dicarbonylrhodium(I) complex, [RhI(indol)$(CO)_2$] by precipitation. The anion formed by double deprotonation of the indole-2-carboxylic acid (indol(H_2)) ligand displays an unprecedented and unexpected mode of coordination with Rh(I) by forming bridging ligand to two rhodium centers; the ketonic oxygen atom coordinating (*κO*) to the Rh2 atom, while the *N,O* atoms bind to a second rhodium atom Rh1 atom in the more familiar bidentate (*κN,O*) fashion. The dinuclear title complex simplifies as [Rh(indol)(CO)$(AsPh_3)$Rh(CO)$(AsPh_3)_2$].[8] [Rh(indol)(CO)$(AsPh_3)$Rh(CO)$(AsPh_3)_2$] was synthesized by dissolving [Rh(indol)$(CO)_2$] (0.0412 g, 0.1291 mmol) in 5 cm^3 of acetone. Triphenylarsine ($AsPh_3$) (0.0396 g, 0.1291 mmol) was added to the solution with stirring, resulting in the immediate evolution of CO gas. After a few minutes the reaction was completed as determined by IR spectroscopy. Ice water was added drop-wise to the solution. A yellow precipitate was filtered off and dried.

Table 1: Data collection and handling.

Crystal:	Yellow cuboid
Size:	0.37 × 0.27 × 0.07 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.28 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	51,426, 14,547, 0.069
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 11,878
$N(param)_{refined}$:	714
Programs:	SHELX[1], Bruker[2], Olex2[3], Diamond[4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Rh1	0.79134 (2)	0.29834 (2)	0.22951 (2)	0.01971 (6)
Rh2	0.42314 (2)	0.12525 (2)	0.27869 (2)	0.01904 (6)
As1	0.71298 (2)	0.39805 (2)	0.15301 (2)	0.02027 (7)
As2	0.49169 (2)	0.28291 (2)	0.37905 (2)	0.01931 (7)
As3	0.33916 (2)	−0.04416 (2)	0.18659 (2)	0.01924 (7)
O1	0.9990 (2)	0.3980 (2)	0.19712 (18)	0.0471 (7)
O2	0.65112 (17)	0.23173 (16)	0.26069 (12)	0.0232 (4)
O3	0.58455 (16)	0.12646 (16)	0.33612 (12)	0.0223 (4)
O4	0.1902 (2)	0.1131 (2)	0.21100 (17)	0.0518 (8)
N1	0.84275 (19)	0.21163 (19)	0.30648 (14)	0.0205 (5)
C1	0.6632 (2)	0.1763 (2)	0.31286 (17)	0.0212 (6)
C2	0.7725 (2)	0.1708 (2)	0.34603 (18)	0.0218 (6)
C3	0.8194 (3)	0.1290 (2)	0.40890 (19)	0.0253 (6)
H3	0.787137	0.097484	0.444932	0.030*
C4	0.9248 (2)	0.1427 (2)	0.40863 (18)	0.0240 (6)
C5	1.0115 (3)	0.1171 (2)	0.45641 (19)	0.0287 (7)
H5	1.006320	0.085424	0.500967	0.034*
C6	1.1040 (3)	0.1388 (3)	0.4375 (2)	0.0306 (7)
H6	1.163540	0.122383	0.469543	0.037*
C7	1.1110 (3)	0.1851 (2)	0.3713 (2)	0.0303 (7)
H7	1.174292	0.197075	0.358341	0.036*
C8	1.0293 (2)	0.2137 (2)	0.32442 (19)	0.0253 (6)
H8	1.036318	0.246394	0.280616	0.030*
C9	0.9357 (2)	0.1930 (2)	0.34368 (17)	0.0213 (6)
C10	0.2808 (3)	0.1173 (2)	0.2359 (2)	0.0308 (7)
C11	0.9166 (3)	0.3578 (3)	0.2086 (2)	0.0290 (7)
C12	0.7400 (3)	0.5181 (2)	0.22645 (18)	0.0241 (6)
C13	0.8495 (3)	0.5752 (3)	0.2960 (2)	0.0365 (8)
H13	0.908498	0.555022	0.306694	0.044*
C14	0.8726 (4)	0.6618 (3)	0.3498 (2)	0.0449 (9)
H14	0.947925	0.701613	0.396792	0.054*
C15	0.7865 (4)	0.6901 (3)	0.3353 (2)	0.0476 (10)
H15	0.802236	0.748914	0.372369	0.057*
C16	0.6776 (4)	0.6328 (3)	0.2667 (2)	0.0419 (9)
H16	0.618339	0.652333	0.256550	0.050*
C17	0.6542 (3)	0.5469 (3)	0.2126 (2)	0.0308 (7)
H17	0.578721	0.507497	0.165719	0.037*
C18	0.7784 (2)	0.4639 (2)	0.07975 (18)	0.0231 (6)
C19	0.8257 (3)	0.5703 (2)	0.0857 (2)	0.0274 (7)
H19	0.825069	0.614220	0.125797	0.033*
C20	0.8747 (3)	0.6138 (3)	0.0329 (2)	0.0340 (8)
H20	0.907139	0.687378	0.037254	0.041*
C21	0.8765 (3)	0.5513 (3)	−0.0252 (2)	0.0390 (8)
H21	0.909904	0.581354	−0.061088	0.047*
C22	0.8295 (4)	0.4446 (3)	−0.0312 (2)	0.0484 (10)
H22	0.831107	0.401158	−0.071177	0.058*
C23	0.7799 (3)	0.4000 (3)	0.0207 (2)	0.0398 (8)
H23	0.747019	0.326360	0.016063	0.048*
C24	0.5437 (2)	0.3325 (2)	0.08146 (17)	0.0218 (6)
C25	0.4995 (3)	0.3683 (3)	0.01218 (19)	0.0304 (7)
H25	0.551845	0.422708	−0.002825	0.036*
C26	0.3771 (3)	0.3232 (3)	−0.0348 (2)	0.0362 (8)
H26	0.346314	0.346630	−0.082478	0.043*
C27	0.3007 (3)	0.2455 (3)	−0.01308 (19)	0.0323 (7)
H27	0.217579	0.216243	−0.045165	0.039*
C28	0.3443 (3)	0.2098 (3)	0.05510 (19)	0.0294 (7)
H28	0.291298	0.155352	0.069613	0.035*
C29	0.4663 (3)	0.2535 (3)	0.10298 (18)	0.0269 (7)
H29	0.496262	0.229094	0.150302	0.032*
C30	0.4131 (2)	0.3624 (2)	0.33181 (18)	0.0215 (6)
C31	0.4105 (3)	0.3836 (3)	0.2565 (2)	0.0318 (7)
H31	0.451373	0.364171	0.233229	0.038*
C32	0.3484 (3)	0.4333 (3)	0.2150 (2)	0.0389 (8)
H32	0.347747	0.448319	0.163832	0.047*
C33	0.2882 (3)	0.4606 (3)	0.2477 (2)	0.0379 (8)
H33	0.245143	0.493853	0.218876	0.045*
C34	0.2899 (3)	0.4400 (3)	0.3223 (2)	0.0345 (8)
H34	0.248039	0.458948	0.344819	0.041*
C35	0.3533 (3)	0.3910 (2)	0.36498 (19)	0.0269 (6)
H35	0.355167	0.377429	0.416752	0.032*
C36	0.6570 (2)	0.3884 (2)	0.44000 (17)	0.0210 (6)
C37	0.6932 (3)	0.4952 (2)	0.45390 (19)	0.0269 (6)
H37	0.636812	0.518203	0.430565	0.032*
C38	0.8130 (3)	0.5690 (3)	0.5024 (2)	0.0336 (7)
H38	0.837583	0.642204	0.512250	0.040*
C39	0.8954 (3)	0.5363 (3)	0.5358 (2)	0.0352 (8)
H39	0.976539	0.586442	0.569097	0.042*
C40	0.8589 (3)	0.4299 (3)	0.52046 (19)	0.0332 (7)
H40	0.915910	0.407193	0.542400	0.040*
C41	0.7400 (3)	0.3553 (3)	0.47335 (18)	0.0262 (6)
H41	0.715788	0.282225	0.464066	0.031*
C42	0.4533 (2)	0.2430 (2)	0.46968 (18)	0.0244 (6)
C43	0.4834 (3)	0.3162 (3)	0.5377 (2)	0.0357 (8)
H43	0.520937	0.389220	0.539648	0.043*
C44	0.4592 (3)	0.2839 (4)	0.6030 (2)	0.0527 (11)
H44	0.477753	0.334305	0.648871	0.063*
C45	0.4073 (3)	0.1768 (4)	0.6009 (2)	0.0563 (13)
H45	0.391054	0.154000	0.645587	0.068*
C46	0.3800 (3)	0.1049 (4)	0.5344 (3)	0.0503 (11)
H46	0.345797	0.032169	0.533497	0.060*
C47	0.4017 (3)	0.1369 (3)	0.4684 (2)	0.0348 (8)
H47	0.381238	0.086077	0.422034	0.042*
C48	0.2750 (2)	−0.1581 (2)	0.23482 (18)	0.0233 (6)
C49	0.3366 (3)	−0.1442 (3)	0.3205 (2)	0.0316 (7)
H49	0.405663	−0.078875	0.353550	0.038*
C50	0.2974 (3)	−0.2251 (3)	0.3572 (2)	0.0406 (9)
H50	0.339251	−0.215627	0.415511	0.049*
C51	0.1964 (3)	−0.3208 (3)	0.3085 (2)	0.0419 (9)
H51	0.169781	−0.376892	0.333527	0.050*
C52	0.1349 (3)	−0.3343 (3)	0.2241 (2)	0.0393 (8)
H52	0.065383	−0.399428	0.191193	0.047*
C53	0.1741 (3)	−0.2530 (3)	0.1869 (2)	0.0289 (7)
H53	0.131633	−0.262605	0.128648	0.035*
C54	0.2119 (2)	−0.0858 (2)	0.07508 (17)	0.0217 (6)
C55	0.2249 (3)	−0.1097 (3)	0.00531 (19)	0.0300 (7)
H55	0.296509	−0.107404	0.012130	0.036*
C56	0.1344 (3)	−0.1370 (3)	−0.0746 (2)	0.0383 (8)
H56	0.144368	−0.152713	−0.122074	0.046*
C57	0.0300 (3)	−0.1411 (3)	−0.0847 (2)	0.0385 (8)
H57	−0.032126	−0.159820	−0.139078	0.046*
C58	0.0163 (3)	−0.1181 (3)	−0.0156 (2)	0.0329 (7)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H58	−0.055649	−0.120977	−0.022696	0.039*
C59	0.1063 (3)	−0.0907 (2)	0.06419 (19)	0.0271 (7)
H59	0.095627	−0.075365	0.111416	0.033*
C60	0.4499 (2)	−0.0702 (3)	0.16362 (18)	0.0271 (7)
C61	0.5205 (3)	0.0054 (3)	0.1352 (2)	0.0371 (8)
H61	0.516667	0.068638	0.131129	0.044*
C62	0.5962 (3)	−0.0118 (4)	0.1130 (2)	0.0477 (10)
H62	0.645535	0.039820	0.094383	0.057*
C63	0.5995 (4)	−0.1046 (4)	0.1182 (2)	0.0615 (14)
H63	0.650718	−0.116966	0.102064	0.074*
C64	0.5303 (4)	−0.1793 (4)	0.1461 (3)	0.0625 (13)
H64	0.533749	−0.242781	0.149316	0.075*
C65	0.4547 (3)	−0.1620 (3)	0.1699 (2)	0.0404 (9)
H65	0.407298	−0.212844	0.190210	0.048*
O00O	0.9584 (3)	0.8245 (2)	0.18113 (17)	0.0591 (8)
C66	1.0860 (3)	0.9061 (3)	0.3235 (2)	0.0496 (10)
H66A	1.126773	0.869169	0.315783	0.074*
H66B	1.062660	0.885824	0.367744	0.074*
H66C	1.139373	0.982386	0.339211	0.074*
C67	0.9784 (3)	0.8770 (3)	0.2440 (2)	0.0374 (8)
C68	0.8977 (3)	0.9164 (3)	0.2465 (3)	0.0570 (12)
H68A	0.933528	0.991875	0.248864	0.085*
H68B	0.884681	0.905010	0.295976	0.085*
H68C	0.821671	0.878145	0.196151	0.085*

Yellow cuboid crystals were obtained from recrystallization in acetone and a few drops of water.

2 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) = 1.2U_{eq}], for methine C–H of 0.98 Å (C–H) [U_{iso}(H) = 1.5U_{eq}]. The graphics were obtained using the DIAMOND[4] program with 50 % probability ellipsoids. The highest peak is located 0.87 Å from As3 and the deepest hole is situated 0.70 Å from Rh2 respectively.

3 Comment

The rhodium(I) complexes and their oxidative additive (RhIII-alkyl) and migratory insertion (RhIII-acyl) products have been extensively studied in the past decade. The precursor $[Rh^{I}(I)_2(CO)_2]^-$ in the Monsanto process is relatively unstable and by manipulating the precursor by introducing different bidentate ligands forming $[Rh(BID)(CO)_2]$ complexes (where BID denote different monocharged bidentate ligands such as 2-oxopyridine N-oxide, 8-hydroxyquinoline, indoline-2-carboxylic acid, etc.) One of the carbonyl ligands in this precursor may be replaced by monophosphine or arsine or stibine ligands to form [Rh(*L*,*L*'-BID)(CO)(AX_3)] complexes (where A = P, As, Sb and X_3 = Ph_3, Ph_2Cy, $PhCy_2$, Cy_3, etc.) Generally, this substitution with asymmetrical bidentate ligands might form two isomers, with complexes where AX_3 is *trans* with respect to the strongest donor atom of the bidentate ligand as the preferred isomer.[5–15] The title complex is isomorphous and isostructural with the corresponding triphenylphospnine complex.[8] The individual $indol^{2-}$ ligand is coordinated to both rhodium atoms in a distorted square planar geometry, as seen in (a) the small 79.61(16)° bite angle of the five membered ring as well the angles C11–Rh1–As: 90.27(18)°, O2–Rh1–As1: 91.36(15)°, C11–Rh1–N1: 98.58(17)°, around Rh1, as well as (b) the angles C10–Rh2–As3: 90.16(17)°, As3–Rh2–O3: 89.40(13)°, O3–Rh2–As2: 92.94(16)°, and As2–Rh2–C19: 86.86(14)° around Rh2, respectively.

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