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Tris(μ-acetato)-μ-[(2-bromophenyl)(*o*-phenylene)phenylphosphine-*C*:*P*]-tricyclohexylphosphinedirhodium(II)

S. García-Granda,* M. R. Díaz and
F. Gómez-Beltrán

*Departamento de Química Física y Analítica,
Facultad de Química, Universidad de Ovideo,
Julián Clavería s/n, 33006-Oviedo, Spain*

E. Peris and P. Lahuerta

*Departament de Química Inorgànica,
Facultad de Química, Universitat de València,
Doctor Moliner, 50, 46100 Burjassot, València, Spain*

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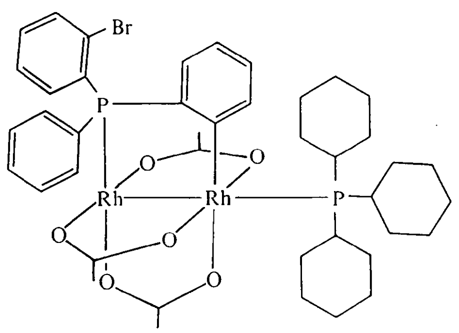
Abstract

The single-crystal X-ray structure determination of the title compound, tris(μ-acetato-O:O)-μ-{2-[(2-bromophenyl)phenylphosphino]phenyl-C^1:P^2}-tricyclohexylphosphine-*P*)dirhodium(II)(*Rh*—*Rh*)-trichloromethane solvate, $[Rh_2(\mu\text{-}C_2H_3O_2)_3(\mu\text{-}C_{18}H_{13}BrP)(C_{18}H_{33}P)].CHCl_3$, is reported. Space group $P1$ was established and the absolute configuration of the title compound was assigned. The Rh_2^{4+} coordination geometry is defined by three bridging acetates, one monometallated triphenylphosphine and one axial tricyclohexylphosphine. The Rh(1) coordination geometry is octahedral, while Rh(2) is pentacoordinated. The Rh(1)—Rh(2) distance is 2.4769 (1) Å. The Rh(2)···Br(1) intermolecular distance is 3.669 (1) Å.

Comment

It is known that rhodium acetate reacts with arylphosphines to give mono- and dimetallated dirhodium(II) compounds. In the course of our investigations several of these compounds have been obtained in which the phosphine ligand bridges the two Rh atoms. We have observed that those compounds which have Cl- and Br-substituted metallated phosphines show a special type of reactivity, which in some cases has cast some light on the reaction pathways for the formation of mono- and dimetallated compounds.

We reacted the phosphine $P(o\text{-}C_6H_4Br)(C_6H_5)_2$ with $Rh_2(O_2CCH_3)_4(MeOH)_2$ and obtained the new monometallated compound $[Rh_2(O_2CCH_3)_3\{(C_6H_4)P(o\text{-}C_6H_4Br)(C_6H_5)\}](HO_2CCH_3)_2$, which in the presence of the phosphine $P(C_6H_{11})_3$ afforded single crystals of $[Rh_2(O_2CCH_3)_3\{(C_6H_4)P(o\text{-}C_6H_4Br)(C_6H_5)\}P(C_6H_{11})_3]$, which were suitable for diffraction analysis. Fig. 1 shows the coordination and the atomic numbering scheme for the title compound (I).



(I)

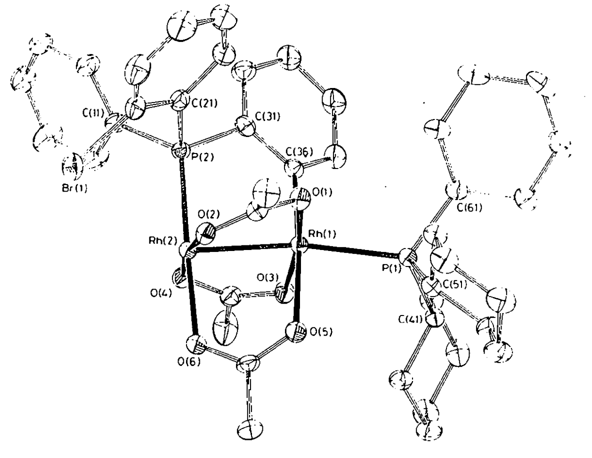


Fig. 1. *EUCLID* (Spek, 1982) diagram showing a view of the title compound and the atomic numbering scheme.

Experimental

Crystal data

$[Rh_2(C_2H_3O_2)_3(C_{18}H_{13}BrP)(C_{18}H_{33}P)].CHCl_3$
M_r = 1122.93
Triclinic
$P1$
a = 9.828 (2) Å
b = 9.922 (2) Å
c = 13.074 (3) Å
α = 84.90 (2)°
β = 69.74 (2)°
γ = 84.52 (2)°
V = 1188.3 (5) Å^3

Z = 1
D_x = 1.57 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 20–23°
μ = 1.79 mm^{-1}
T = 293 K
Prismatic
0.50 × 0.33 × 0.26 mm
Brown

Data collection

Enraf-Nonius CAD-4 diffractometer

R_{int} = 0.025
θ_{max} = 25°

$\omega/2\theta$ scans
Absorption correction:
empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.72$, $T_{max} = 1.18$
10 494 measured reflections
9205 independent reflections
8741 observed reflections
$[I > 3\sigma(I)]$

$h = -12 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -12 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity variation: 0.98-1.06%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.037$
$S = 2.0142$
8741 reflections
653 parameters
$w = 1/[\sigma^2(F_o) + 0.00040F_o^2]$

$(\Delta/\sigma)_{max} = 0.4$
$\Delta\rho_{max} = 1.94$ e Å^{-3}
$\Delta\rho_{min} = -1.49$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rh(1)	−0.05746 (4)	0.09512 (4)	−0.16317 (3)	0.02530 (9)
Rh(2)	0.000	0.000	0.000	0.0284 (1)
Br(1)	0.02034 (7)	0.12992 (7)	0.24810 (5)	0.0515 (2)
P(1)	−0.0556 (1)	0.1857 (1)	−0.34005 (8)	0.0263 (3)
P(2)	−0.2000 (1)	0.1061 (1)	0.10530 (8)	0.0283 (3)
O(1)	−0.0051 (4)	0.2763 (3)	−0.1266 (3)	0.034 (1)
O(2)	0.1103 (3)	0.1703 (3)	−0.0168 (2)	0.034 (1)
O(3)	−0.0965 (4)	−0.0983 (3)	−0.1808 (3)	0.037 (1)
O(4)	−0.0967 (4)	−0.1717 (4)	−0.0117 (3)	0.037 (1)
O(5)	0.1810 (4)	0.0467 (4)	−0.2435 (3)	0.039 (1)
O(6)	0.1937 (4)	−0.0942 (4)	−0.1036 (3)	0.042 (1)
C(1)	0.0812 (6)	0.2720 (5)	−0.0739 (4)	0.036 (1)
C(2)	0.1560 (7)	0.3989 (6)	−0.0760 (5)	0.055 (2)
C(3)	−0.1126 (6)	−0.1867 (5)	−0.1018 (4)	0.037 (2)
C(4)	−0.155 (1)	−0.3237 (7)	−0.1196 (6)	0.072 (3)
C(5)	0.2451 (5)	−0.0445 (6)	−0.2005 (4)	0.040 (2)
C(6)	0.3969 (7)	−0.0992 (8)	−0.2667 (5)	0.065 (2)
C(11)	−0.3053 (5)	0.0170 (4)	0.2330 (3)	0.033 (1)
C(12)	−0.3150 (8)	−0.1211 (6)	0.2338 (5)	0.056 (2)
C(13)	−0.4024 (9)	−0.1917 (7)	0.3272 (5)	0.067 (3)
C(14)	−0.4819 (7)	−0.1236 (6)	0.4171 (4)	0.053 (2)
C(15)	−0.4674 (7)	0.0128 (6)	0.4207 (4)	0.054 (2)
C(16)	−0.3805 (6)	0.0828 (5)	0.3274 (4)	0.046 (2)
C(21)	−0.1775 (5)	0.2705 (4)	0.1497 (3)	0.035 (1)
C(22)	−0.0820 (6)	0.2832 (5)	0.2075 (4)	0.041 (1)
C(23)	−0.0627 (8)	0.4109 (6)	0.2361 (5)	0.059 (2)
C(24)	−0.138 (1)	0.5236 (6)	0.2094 (6)	0.077 (3)
C(25)	−0.2311 (9)	0.5143 (5)	0.1562 (6)	0.062 (2)
C(26)	−0.2522 (7)	0.3884 (5)	0.1247 (4)	0.047 (2)
C(31)	−0.3277 (5)	0.1382 (5)	0.0332 (4)	0.034 (1)
C(32)	−0.4764 (6)	0.1616 (6)	0.0882 (4)	0.045 (2)
C(33)	−0.5766 (5)	0.1635 (6)	0.0339 (4)	0.051 (2)
C(34)	−0.5255 (5)	0.1347 (6)	−0.0745 (5)	0.049 (2)
C(35)	−0.3774 (5)	0.1096 (5)	−0.1293 (4)	0.039 (1)
C(36)	−0.2722 (4)	0.1206 (4)	−0.0804 (3)	0.030 (1)
C(41)	−0.0411 (5)	0.0513 (4)	−0.4353 (3)	0.030 (1)
C(42)	0.0905 (6)	−0.0510 (5)	−0.4421 (4)	0.038 (1)
C(43)	0.1102 (7)	−0.1492 (5)	−0.5303 (5)	0.050 (2)
C(44)	−0.0279 (8)	−0.2254 (5)	−0.5048 (5)	0.057 (2)
C(45)	−0.1573 (6)	−0.1280 (5)	−0.4966 (5)	0.046 (2)
C(46)	−0.1796 (6)	−0.0225 (5)	−0.4094 (4)	0.041 (2)
C(51)	0.1137 (4)	0.2780 (4)	−0.4086 (3)	0.032 (1)
C(52)	0.0983 (5)	0.4219 (5)	−0.3691 (4)	0.037 (1)
C(53)	0.2435 (6)	0.4877 (6)	−0.4100 (5)	0.050 (2)
C(54)	0.3088 (7)	0.4921 (6)	−0.5344 (6)	0.057 (2)
C(55)	0.3225 (6)	0.3510 (6)	−0.5748 (5)	0.054 (2)
C(56)	0.1776 (6)	0.2815 (6)	−0.5339 (4)	0.043 (2)
C(61)	−0.2118 (5)	0.2991 (4)	−0.3512 (4)	0.035 (1)
C(62)	−0.2642 (6)	0.4086 (5)	−0.2664 (5)	0.044 (2)
C(63)	−0.4108 (6)	0.4768 (7)	−0.2701 (6)	0.059 (2)
C(64)	−0.3985 (7)	0.5382 (6)	−0.3829 (6)	0.061 (2)
C(65)	−0.3460 (7)	0.4322 (7)	−0.4656 (6)	0.059 (2)
C(66)	−0.2002 (6)	0.3627 (6)	−0.4654 (5)	0.045 (2)
Cl(1)	0.3591 (8)	−0.4370 (6)	0.0675 (7)	0.233 (5)
Cl(2)	0.4402 (8)	−0.1930 (5)	0.103 (1)	0.334 (9)
Cl(3)	0.1402 (6)	−0.2185 (6)	0.1647 (4)	0.184 (3)
C(10)	0.312 (1)	−0.262 (1)	0.0712 (9)	0.113 (5)

Table 2. *Selected geometric parameters* (Å, °)

Rh(1)—Rh(2)	2.4769 (7)	Rh(2)—O(2)	2.049 (3)
Rh(1)—O(3)	2.040 (3)	Br(1)—C(22)	1.882 (5)
Rh(2)—P(2)	2.203 (1)	Rh(1)—O(1)	2.055 (3)
Rh(2)—O(6)	2.105 (3)	Rh(1)—C(36)	2.014 (4)
Rh(1)—P(1)	2.400 (1)	Rh(2)—O(4)	2.070 (4)
Rh(1)—O(5)	2.235 (3)	Rh(2)—Br(1)	3.669 (1)
P(1)—Rh(1)—Rh(2)	167.26 (8)	O(1)—Rh(1)—Rh(2)	85.0 (1)
O(1)—Rh(1)—P(1)	92.0 (1)	O(3)—Rh(1)—Rh(2)	85.9 (1)
O(3)—Rh(1)—P(1)	96.5 (1)	O(3)—Rh(1)—O(1)	170.8 (1)
O(5)—Rh(1)—Rh(2)	81.4 (1)	O(5)—Rh(1)—P(1)	86.0 (1)
O(5)—Rh(1)—O(1)	87.1 (1)	O(5)—Rh(1)—O(3)	90.1 (1)
C(36)—Rh(1)—Rh(2)	93.6 (1)	C(36)—Rh(1)—P(1)	99.1 (1)
C(36)—Rh(1)—O(1)	96.0 (2)	C(36)—Rh(1)—O(3)	86.0 (2)
C(36)—Rh(1)—O(5)	173.9 (1)	P(2)—Rh(2)—Rh(1)	89.68 (6)
O(2)—Rh(2)—Rh(1)	85.9 (1)	O(2)—Rh(2)—P(2)	90.1 (1)
O(4)—Rh(2)—Rh(1)	86.6 (1)	O(4)—Rh(2)—P(2)	96.1 (1)
O(4)—Rh(2)—O(2)	170.2 (1)	O(6)—Rh(2)—Rh(1)	89.2 (1)
O(6)—Rh(2)—P(2)	177.8 (1)	O(6)—Rh(2)—O(2)	88.0 (1)
O(6)—Rh(2)—O(4)	85.7 (1)		

Profile analysis was performed on all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Additional empirical absorption correction was applied after the isotropic stage of the refinement. The H atoms were located by difference Fourier synthesis and refined isotropically. The absolute configuration was checked with a new version of *BIJVOET* (Beurskens, Noordik & Beurskens, 1980), which gave $B = 0.998$ (1) for the 1291 strongest Friedel pairs. Maximum and minimum $\Delta\rho$ were near to the Rh and Br atoms. The rest of the peaks were less than 0.60 e Å^{-3}. All calculations were performed on a MicroVAX 3400 at the Scientific Computer Centre of the University of Oviedo. The programs used were *DATAR* (local program), *SHELX*76 (Sheldrick, 1976), *DIRDIF* (Beurskens *et al.*, 1992), *SHELXS*86 (Sheldrick, 1985), *EUCLID* (Spek, 1982) and *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71718 (74 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1056]

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Trichlorobis(tetrahydrofuran)indium(III)

Bruce R. Whittlesey and
Ittycheriah P. Ittycheriah

*Department of Chemistry and Biochemistry,
Texas Tech University, Lubbock, Texas 79409, USA*

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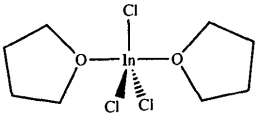
Abstract

The coordination geometry about the In atom in trichlorobis(tetrahydrofuran)indium(III), [InCl$_3$(C$_4$H$_8$O)$_2$], approximates a trigonal bipyramid, with three Cl atoms in equatorial positions and two axial tetrahydrofuran ligands. The molecule lies on a crystallographic twofold axis that is coincident with one of the In—Cl bonds.

Comment

Recent interest in the preparation of semiconducting materials has led to widespread activity in the synthesis of new compounds of indium. A common starting material for these preparations is indium trichloride and the reactions are often carried out with tetrahydrofuran as the solvent. In the course of our synthetic investigations we were able to isolate crystals of the complex InCl$_3$(thf)$_2$ (I) (thf = tetrahydrofuran). Indium complexes exhibit a wide range of coordination numbers and geometries, and the empirical formula of the complex is not always a reliable indicator of its structure. The InCl$_5^{2-}$ ion has a square-pyramidal configuration (Brown, Einstein & Tuck, 1969), whereas InCl$_3$(PPh$_3$)$_2$ has trigonal bipyramidal geometry (Veidis & Palenik, 1969). In the case of InI$_3$(Me$_2$SO)$_2$ the crystal structure determination revealed that the compound is actually the ionic complex [InI$_2$(Me$_2$SO)$_4$][InI$_4$] (Einstein & Tuck, 1970). We decided, therefore, to undertake a single-crystal X-ray diffraction study of InCl$_3$(thf)$_2$ in order to determine the exact structure of this synthetic intermediate. The parameters obtained from the structure determination also provide a benchmark for comparison with similar structural elements in other complexes in which Cl or thf ligands are attached to In.



(I)

A colorless crystal of InCl$_3$(thf)$_2$ was obtained from a solution of indium trichloride in dry tetrahydrofuran and was sealed in a 0.5 mm glass capillary tube under a thf-saturated atmosphere of dry nitrogen. The structure determination revealed that the coordination geometry about the In atom approximates a trigonal bipyramid, with the three Cl atoms in equatorial positions and two axial thf ligands. The molecule lies on a crystallographic twofold axis that passes through the In and Cl(1) atoms. Both of the symmetry-related thf ligands are oriented so that the C$_4$O rings are tilted toward the In—Cl(1) bond and are rotated slightly about the oxygen–centroid axis, with ring-centroid—O—In—Cl(1) torsion angles of 3.1°. Each In—O bond axis makes an angle of 112.5° with respect to the mean plane of the ring, the In—O—centroid angle is 155.8° and the sum of the angles about the O atom is 351.2 (7)°. The relationship of the two O atoms to the In is virtually linear, with a O—In—O′ angle of 179.0 (3)°. The In—O distance is 2.265 (5) Å.

The orientations of the thf ligands cause very little distortion from idealized local D_{3h} symmetry at the In atom. The Cl(2)—In—Cl(2′) angle of 118.1 (1)° and the value of 120.9 (1)° for the two identical Cl(1)—In—Cl(2) angles are very close to the idealized value of 120°, and the In—Cl(1) bond distance of 2.314 (3) Å is only slightly shorter than the value of 2.339 (2) Å observed for the bonds to the two symmetry-related Cl atoms.

Coordination geometry and electronic factors appear to have a significant effect upon the In—Cl bond length. Higher coordination numbers and bulky ligands are expected to give longer bonds as a result of steric crowding at the In atom. Greater negative charge and increased electron donation from ligands should also increase the In—Cl distance. The average In—Cl distance of 2.331 (3) Å for InCl$_3$(thf)$_2$ is virtually the same as the value of 2.33 (3) Å found for the InCl$_4^-$ anion, which has a lower coordination number but a higher negative charge (Trotter, Einstein & Tuck, 1969). The effects of increasing coordination number and increasing negative charge are evident when comparing these values to those found for the anionic complexes InCl$_5^{2-}$ [square-pyramidal geometry, average In—Cl