

C(10)	0.1900 (17)	0.0061 (18)	0.1387 (21)	0.085 (7)
C(11)	0.4438 (21)	0.0875 (27)	0.2108 (27)	0.173
C(12)	0.3773 (21)	−0.0389 (20)	0.3246 (23)	0.127
C(13)	0.3266 (29)	0.1545 (20)	0.4002 (24)	0.152
W'	0.74095 (7)	0.36181 (7)	0.17686 (8)	0.057
Si(1)'	0.61259 (56)	0.54570 (52)	0.28445 (67)	0.088
Si(2)'	0.84664 (65)	0.32599 (50)	0.62146 (69)	0.090
N(1)'	0.7875 (19)	0.4431 (19)	0.1432 (18)	0.108
N(2)'	0.8605 (16)	0.4027 (13)	0.4512 (17)	0.069 (5)
N(3)'	0.9378 (15)	0.3891 (15)	0.4110 (19)	0.094
O(1)'	0.8313 (20)	0.4988 (15)	0.1083 (19)	0.149
O(2)'	0.7541 (11)	0.3960 (9)	0.3683 (12)	0.066
O(3)'	0.9088 (10)	0.3691 (12)	0.2900 (15)	0.085
C(1)'	0.5914 (16)	0.4205 (16)	0.1894 (18)	0.075
C(2)'	0.5881 (19)	0.2396 (18)	0.0231 (22)	0.092 (5)
C(3)'	0.6560 (19)	0.2636 (17)	−0.0387 (21)	0.086 (7)
C(4)'	0.7598 (16)	0.2412 (16)	0.0115 (20)	0.070 (6)
C(5)'	0.7570 (20)	0.2057 (18)	0.0915 (23)	0.095 (8)
C(6)'	0.6510 (20)	0.2017 (18)	0.0993 (23)	0.092 (8)
Cp'	0.6824	0.2304	0.0373	0.09
C(7)'	0.7470 (24)	0.6039 (20)	0.4182 (28)	0.156
C(8)'	0.5945 (47)	0.6044 (25)	0.1810 (34)	0.320
C(9)'	0.4977 (32)	0.5673 (26)	0.3439 (58)	0.380
C(10)'	0.8715 (16)	0.4277 (16)	0.5835 (20)	0.075 (7)
C(11)'	0.7251 (37)	0.2510 (32)	0.5168 (33)	0.272
C(12)'	0.8493 (24)	0.3697 (17)	0.7850 (22)	0.107
C(13)'	0.9744 (34)	0.2675 (31)	0.6076 (41)	0.232

Table 2. Selected geometric parameters (Å)

W—N(1)	1.76 (2)	W'—N(1)'	1.62 (3)
W—O(2)	2.12 (2)	W'—O(2)'	2.13 (1)
W—O(3)	2.15 (1)	W'—O(3)'	2.11 (1)
W—C(1)	2.19 (2)	W'—C(1)'	2.19 (2)
W—C(2)	2.38 (2)	W'—C(2)'	2.37 (2)
W—C(3)	2.26 (2)	W'—C(3)'	2.34 (2)
W—C(4)	2.31 (2)	W'—C(4)'	2.31 (2)
W—C(5)	2.37 (2)	W'—C(5)'	2.38 (2)
W—C(6)	2.44 (2)	W'—C(6)'	2.43 (2)
W—Cp	2.04	W'—Cp'	2.06
Si(1)—C(1)	1.88 (2)	Si(1)'—C(1)'	1.86 (2)
Si(2)—C(10)	1.94 (2)	Si(2)'—C(10)'	1.88 (2)
N(1)—O(1)	1.23 (2)	N(1)'—O(1)'	1.28 (2)
N(2)—N(3)	1.23 (2)	N(2)'—N(3)'	1.22 (2)
N(2)—O(2)	1.29 (2)	N(2)'—O(2)'	1.38 (2)
N(2)—C(10)	1.47 (3)	N(2)'—C(10)'	1.46 (2)
N(3)—O(3)	1.31 (2)	N(3)'—O(3)'	1.30 (2)

Three standard reflections decayed to an average 32% of the initial intensities and the data were scaled accordingly; a similar decay was reported for the related compound [WMe₄{ON(Me)NO₂}] (Fletcher & Skapski, 1973). The structure was determined by Patterson methods. Some large displacement parameters for the peripheral atoms indicate possible disorder. Anisotropic displacement parameters for N(2), N(2)', C(10) and C(10)', although not large, were physically unrealistic, and these atoms were treated isotropically in the final least-squares cycles, as were the cyclopentadienyl C atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local program. Program(s) used to refine structure: *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *ORTEPII* (Johnson, 1976).

We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1148). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diiodobis(isopropyldiphenylphosphine oxide-O)cobalt(II)

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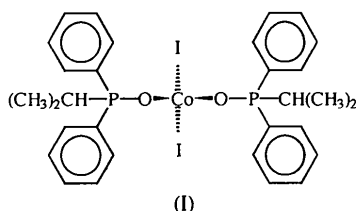
Abstract

The title compound, [CoI₂{(C₆H₅)₂(C₃H₇)OP}₂]₂, contains a four-coordinate Co atom in a distorted tetrahedral coordination environment. Bond lengths are: Co—I 2.558 (1) and 2.593 (2) Å, Co—O 1.958 (6) and 1.946 (6) Å. Angles at the Co atom are: I—Co—I 117.11 (5), O—Co—O 102.7 (3)°.

Comment

Relatively few structures of phosphine oxide complexes of cobalt(II) have been reported. In (Ph₃PO)₂CoCl₂ the metal has distorted tetrahedral coordination with Cl—Co—Cl 114.0 (1) and O—Co—O 96.4 (3)° (Mangion, Smith & Shore, 1976). Spectroscopic studies suggest similar structures for the bromo and iodo analogues (Pierrard, Rimbault & Hugel, 1976, 1982). Complexes of cobalt(II) nitrate, (R₃PO)₂Co(NO₃)₂, contain bidentate nitrate groups and *cis*-phosphine oxides, with pseudo-octahedral coordination at the Co atom for R = Ph (Dias Rodrigues, Francisco & Lechat, 1982) or R = Et (Alnaji, Dartigueanave, Dartigueanave, Simard & Beauchamp, 1991).

As part of an investigation of phosphine complexes of cobalt halides, we studied the interaction of CoI₂ with isopropyldiphenylphosphine. A structural investigation of the product showed that air oxidation had occurred to give the 2:1 complex, (I), of the phosphine oxide.



The complex forms molecular units in which the Co atom is in a distorted tetrahedral environment. The Co—I bond lengths are 2.558 (1) and 2.593 (2) Å, 17% longer than the Co—Cl bond lengths of 2.203 (3) and 2.203 (4) Å found in $(\text{Ph}_3\text{PO})_2\text{CoCl}_2$. Correspondingly, the larger halogen forces an increase in the bond angle about Co to 117.11 (5)° for I—Co—I from 114.0 (1)° for Cl—Co—Cl. The Co—O bond lengths are 1.958 (6) and 1.946 (6) Å, similar to those reported for other phosphine oxide complexes of cobalt(II), and the O—Co—O angle is 102.7 (3)°. We found Co—O—P angles of 157.9 (4) and 169.4 (5)°; a considerable variation of this angle has been reported for coordinated phosphine oxides.

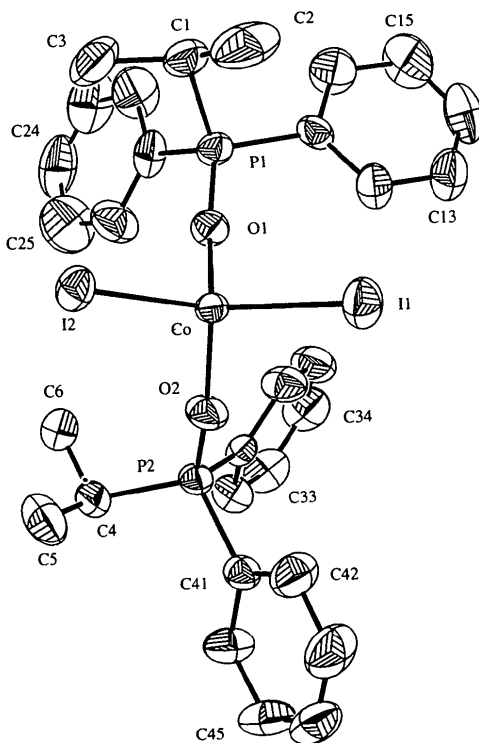


Fig. 1. A view of the molecule with 40% probability displacement ellipsoids, showing the atom-numbering scheme; phenyl ring atoms are numbered C*i*1–C*i*6 (*i* = 1–4). H atoms are omitted.

Experimental

A solution of CoI_2 in ethanol was prepared by mixing ethanolic $\text{CoCl}_2(\text{H}_2\text{O})_6$ and NaI in a 1:2 ratio, removing NaCl by filtration, and reducing volume by vacuum evaporation. A

stoichiometric amount of $(\text{CH}_3)_2\text{CH}(\text{C}_6\text{H}_5)_2\text{P}$ was added and the solution stirred for 1 h. Evaporation gave a dark green product, recrystallized from ethanol. Analysis: found C 45.70, H 4.28, P 7.20%; calculated (for $\text{C}_{30}\text{H}_{34}\text{CoI}_2\text{O}_2\text{P}_2$) C 44.96, H 4.25, P 7.73%. Data crystals were grown by diffusion using benzene with hexanes. The density D_m was measured by neutral buoyancy in CCl_4 and hexanes. Because of accidental loss of the crystal used for data collection, its dimensions were not measured.

Crystal data

$[\text{CoI}_2(\text{C}_{15}\text{H}_{17}\text{OP})_2]$

$M_r = 801.24$

Monoclinic

$P2_1$

$a = 10.497$ (2) Å

$b = 17.505$ (6) Å

$c = 9.903$ (3) Å

$\beta = 113.46$ (5)°

$V = 1669.3$ (8) Å³

$Z = 2$

$D_x = 1.594$ Mg m⁻³

$D_m = 1.567$ (2) Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 22

reflections

$\theta = 10\text{--}15^\circ$

$\mu = 2.483$ mm⁻¹

$T = 293$ (2) K

Irregular block

Dark green

Data collection

Enraf–Nonius CAD-4F

diffractometer

$\theta/2\theta$ scans, moving

backgrounds

Absorption correction:

ψ scans (North, Phillips
& Mathews, 1968)

$T_{\min} = 0.92$, $T_{\max} = 1.00$

4327 measured reflections

4042 independent reflections

3449 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0160$

$\theta_{\max} = 24.98^\circ$

$h = 0 \rightarrow 12$

$k = -14 \rightarrow 20$

$l = -11 \rightarrow 10$

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0354$

$wR(F^2) = 0.0965$

$S = 1.060$

4039 reflections

334 parameters

H atoms: riding

$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2$
 $+ 0.6939P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.028$

$\Delta\rho_{\max} = 0.543$ e Å⁻³

$\Delta\rho_{\min} = -0.785$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*
for Crystallography (1992),
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Absolute configuration:

Flack (1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

	$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
I1	0.28917 (7)	0.32379 (4)	0.22220 (8)	0.0688 (2)
I2	0.58368 (6)	0.25003 (4)	0.65936 (6)	0.0542 (2)
Co	0.35880 (11)	0.22413 (6)	0.42800 (11)	0.0346 (3)
P1	0.0895 (2)	0.22514 (15)	0.5343 (2)	0.0449 (6)
P2	0.3711 (3)	0.04880 (14)	0.2845 (3)	0.0433 (6)
O1	0.2007 (6)	0.2066 (3)	0.4817 (6)	0.048 (2)
O2	0.3733 (7)	0.1278 (4)	0.3370 (7)	0.060 (2)
C1	0.1327 (12)	0.3034 (7)	0.6628 (11)	0.065 (3)
C2	0.1557 (19)	0.3756 (7)	0.5896 (17)	0.113 (5)
C3	0.2553 (13)	0.2823 (8)	0.8030 (12)	0.094 (4)

C4	0.4757 (11)	-0.0136 (7)	0.4297 (11)	0.065 (3)
C5	0.6224 (12)	0.0161 (7)	0.5025 (14)	0.084 (4)
C6	0.4095 (15)	-0.0230 (9)	0.5381 (13)	0.091 (4)
C11	-0.0685 (8)	0.2516 (7)	0.3817 (9)	0.050 (2)
C12	-0.0689 (9)	0.2558 (7)	0.2425 (9)	0.061 (3)
C13	-0.1863 (11)	0.2761 (7)	0.1253 (11)	0.080 (4)
C14	-0.3079 (12)	0.2889 (8)	0.1411 (15)	0.096 (4)
C15	-0.3090 (11)	0.2870 (10)	0.2757 (16)	0.113 (6)
C16	-0.1898 (10)	0.2657 (9)	0.3975 (12)	0.092 (4)
C21	0.0590 (9)	0.1420 (6)	0.6266 (10)	0.059 (3)
C22	-0.0262 (13)	0.1422 (8)	0.7017 (14)	0.099 (5)
C23	-0.0470 (15)	0.0760 (10)	0.7669 (16)	0.112 (6)
C24	0.0210 (18)	0.0121 (9)	0.7657 (16)	0.113 (6)
C25	0.1083 (19)	0.0126 (8)	0.698 (2)	0.131 (6)
C26	0.1260 (13)	0.0762 (6)	0.6245 (15)	0.085 (4)
C31	0.1939 (9)	0.0136 (5)	0.2106 (9)	0.044 (2)
C32	0.1630 (9)	-0.0621 (6)	0.1680 (11)	0.060 (3)
C33	0.0273 (12)	-0.0853 (6)	0.1111 (12)	0.073 (3)
C34	-0.0766 (12)	-0.0365 (8)	0.0985 (14)	0.085 (4)
C35	-0.0458 (11)	0.0360 (7)	0.1453 (14)	0.079 (4)
C36	0.0878 (10)	0.0623 (6)	0.1964 (12)	0.066 (3)
C41	0.4377 (9)	0.0455 (5)	0.1427 (9)	0.047 (2)
C42	0.4613 (13)	0.1114 (6)	0.0827 (12)	0.080 (4)
C43	0.5156 (14)	0.1105 (8)	-0.0221 (13)	0.094 (4)
C44	0.5452 (13)	0.0448 (8)	-0.0707 (13)	0.080 (4)
C45	0.5188 (12)	-0.0215 (8)	-0.0178 (13)	0.081 (4)
C46	0.4685 (12)	-0.0229 (6)	0.0910 (12)	0.069 (3)

Table 2. Selected geometric parameters (Å, °)

I1—Co	2.558 (1)	P2—O2	1.475 (7)
I2—Co	2.593 (2)	P2—C4	1.791 (11)
Co—O2	1.946 (6)	P2—C41	1.802 (9)
Co—O1	1.958 (6)	P2—C31	1.814 (9)
P1—O1	1.491 (6)	C1—C3	1.52 (2)
P1—C1	1.800 (11)	C1—C2	1.52 (2)
P1—C11	1.805 (8)	C4—C6	1.50 (2)
P1—C21	1.814 (9)	C4—C5	1.51 (2)
O2—Co—O1	102.7 (3)	C41—P2—C31	109.1 (4)
O2—Co—I1	105.8 (2)	P1—O1—Co	157.9 (4)
O1—Co—I1	108.6 (2)	P2—O2—Co	169.4 (5)
O2—Co—I2	110.4 (2)	C3—C1—C2	113.6 (11)
O1—Co—I2	111.1 (2)	C3—C1—P1	110.2 (8)
I1—Co—I2	117.11 (5)	C2—C1—P1	109.8 (7)
O1—P1—C1	113.7 (4)	C6—C4—C5	111.8 (10)
O1—P1—C11	110.5 (4)	C6—C4—P2	109.3 (8)
C1—P1—C11	106.6 (5)	C5—C4—P2	110.9 (9)
O1—P1—C21	108.7 (4)	C16—C11—P1	122.6 (7)
C1—P1—C21	107.5 (5)	C12—C11—P1	119.2 (6)
C11—P1—C21	109.9 (4)	C26—C21—P1	118.6 (7)
O2—P2—C4	111.7 (5)	C22—C21—P1	123.6 (9)
O2—P2—C41	110.4 (4)	C36—C31—P2	119.6 (6)
C4—P2—C41	107.6 (5)	C32—C31—P2	121.6 (7)
O2—P2—C31	109.3 (4)	C42—C41—P2	120.3 (7)
C4—P2—C31	108.7 (5)	C46—C41—P2	122.3 (7)

Since the compound crystallizes in a polar space group, polar axis restraints were applied by the method of Flack & Schwarzenbach (1988). Refinement was on F^2 for all reflections, omitting ($\bar{1}$,11,1), (0, $\bar{1}$ 2,1) and ($\bar{1}$,13,1) due to large negative F^2 values. All non-H atoms were assigned anisotropic displacement parameters. Restraints were used to impose planar twofold symmetry upon phenyl rings. Methyl H-atom positions (C—H 0.95 Å) were optimized by a difference Fourier process before each series of cycles, and phenyl H atoms were included in calculated positions (C—H 0.90 Å). A riding model was used for all H atoms, with isotropic Debye factors 110% of those of the attached C atoms. The absolute structure of the crystal was determined by the method of Flack (1983).

Data collection: CAD-4F diffractometer software (Enraf-Nonius, 1982). Cell refinement: CAD-4F diffractometer software. Data reduction: *SDP-Plus* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SDP-Plus*. Program(s) used

to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1993). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dimethylacetonylsulfonium Tetrachlorobis(dimethyl sulfoxide-S)rhodate(III)

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Abstract

The title compound, (C₅H₁₁OS)[RhCl₄(C₂H₆OS)₂], is built up of [(CH₃)₂SCH₂C(O)CH₃]⁺ cations and [RhCl₄{(CH₃)₂SO}₂][−] anions held together by van der Waals forces. The sulfonium cation is derived from an unprecedented deoxygenation reaction of dimethyl sulfoxide. The Rh^{III} atom has a nearly octahedral environment, including two *trans* S-bonded sulfoxide ligands (dmsos-S).