| | | | |
|---|---|---|---|
| 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 (10) | 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: *ORTEP*II (Johnson, 1976).

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## References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fletcher, S. R., Shortland, A., Skapski, A. C. & Wilkinson, G. (1972). *Chem. Commun.* pp. 922–923.

Fletcher, S. R. & Skapski, A. C. (1973). *J. Organomet. Chem.* **59**, 299–307.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Legzdins, P., Rettig, S. J. & Sánchez, L. (1988). *Organometallics*, **7**, 2394–2403.

# Diiodobis(isopropyldiphenylphosphine oxide-*O*)cobalt(II)

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## Abstract

The title compound, [CoI₂{(C₆H₅)₂(C₃H₇)OP}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.

(I)
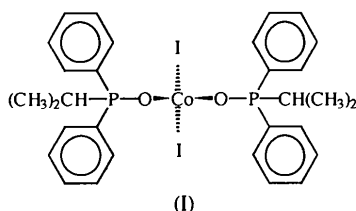
The complex forms molecular units in which the Co atom is in a distorted tetrahedral environment. The Co—I bond lengths are 2.558 (1) and 2.593 (2) Å, 17% longer than the Co—Cl bond lengths of 2.203 (3) and 2.203 (4) Å found in $(Ph_3PO)_2CoCl_2$. Correspondingly, the larger halogen forces an increase 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.
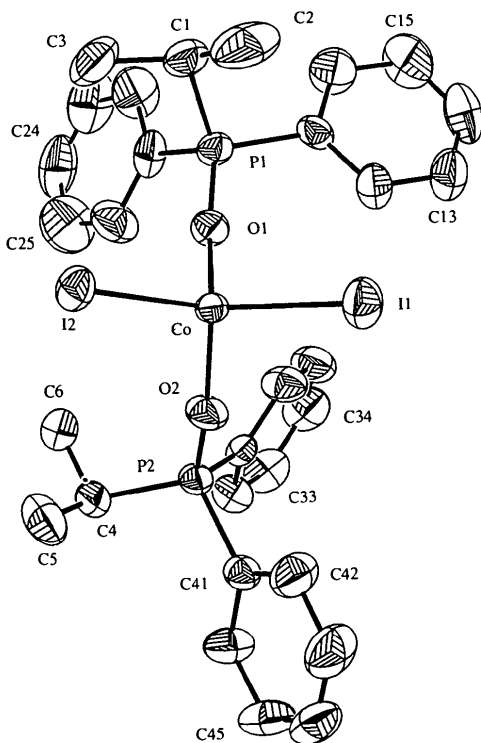


Fig. 1. A view of the molecule with 40% probability displacement ellipsoids, showing the atom-numbering scheme; phenyl ring atoms are numbered Ci1–Ci6 (i = 1–4). H atoms are omitted.

## Experimental

A solution of $CoI_2$ in ethanol was prepared by mixing ethanolic $CoCl_2(H_2O)_6$ and NaI in a 1:2 ratio, removing NaCl by filtration, and reducing volume by vacuum evaporation. A stoichiometric amount of $(CH_3)_2CH(C_6H_5)_2P$ 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 $C_{30}H_{34}CoI_2O_2P_2$) 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

| | |
|---|---|
| $[CoI_2(C_{15}H_{17}OP)_2]$ | Mo $K\alpha$ radiation |
| $M_r = 801.24$ | $\lambda = 0.71073$ Å |
| Monoclinic | Cell parameters from 22 |
| $P2_1$ | reflections |
| $a = 10.497 (2)$ Å | $\theta = 10–15°$ |
| $b = 17.505 (6)$ Å | $\mu = 2.483$ mm$^{-1}$ |
| $c = 9.903 (3)$ Å | $T = 293 (2)$ K |
| $\beta = 113.46 (5)°$ | Irregular block |
| $V = 1669.3 (8)$ Å$^3$ | Dark green |
| $Z = 2$ | |
| $D_x = 1.594$ Mg m$^{-3}$ | |
| $D_m = 1.567 (2)$ Mg m$^{-3}$ | |

### Data collection

| | |
|---|---|
| Enraf–Nonius CAD-4F diffractometer | 3449 observed reflections $[I > 2\sigma(I)]$ |
| $\theta/2\theta$ scans, moving backgrounds | $R_{int} = 0.0160$ $\theta_{max} = 24.98°$ |
| Absorption correction: | $h = 0 \rightarrow 12$ |
| $\psi$ scans (North, Phillips & Mathews, 1968) | $k = -14 \rightarrow 20$ $l = -11 \rightarrow 10$ |
| $T_{min} = 0.92$, $T_{max} = 1.00$ | 3 standard reflections |
| 4327 measured reflections | frequency: 120 min |
| 4042 independent reflections | intensity decay: none |

### Refinement

| | |
|---|---|
| Refinement on $F^2$ | $\Delta\rho_{max} = 0.543$ e Å$^{-3}$ |
| $R[F^2 > 2\sigma(F^2)] = 0.0354$ | $\Delta\rho_{min} = -0.785$ e Å$^{-3}$ |
| $wR(F^2) = 0.0965$ | Extinction correction: none |
| $S = 1.060$ | Atomic scattering factors |
| 4039 reflections | from International Tables |
| 334 parameters | for Crystallography (1992, |
| H atoms: riding | Vol. C, Tables 4.2.6.8 and |
| $w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.6939P]$ | 6.1.1.4) |
| where $P = (F_o^2 + 2F_c^2)/3$ | Absolute configuration: Flack (1983) |
| $(\Delta/\sigma)_{max} = 0.028$ | |

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 | $U_{eq}$ |
|---|---|---|---|---|
| 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 ($\bar{1},11,1$), ($0,\bar{12},1$) 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*.

### References

Alnaji, O., Dartigueanave, M., Dartigueanave, Y., Simard, M. & Beauchamp, A. L. (1991). *Inorg. Chim. Acta*, **187**, 31–38.
Dias Rodrigues, A. M. G., Francisco, R. H. & Lechat, J. R. (1982). *Cryst. Struct. Commun.* **11**, 847–852.
Enraf–Nonius (1982). *CAD-4F User's Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Enraf–Nonius (1985). *Structure Determination Package. SDP-Plus*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* **A44**, 499–506.
Mangion, M. M., Smith, R. & Shore, S. G. (1976). *Cryst. Struct. Commun.* **5**, 493–500.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Pierrard, J.-C., Rimbault, J. & Hugel, R. P. (1976). *Bull. Soc. Chim. Fr.* pp. 11–12, 1711–1714.
Pierrard, J.-C., Rimbault, J. & Hugel, R. P. (1982). *J. Chem. Res. Synop.* pp. 332–333.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Siemens (1993). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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

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## Abstract

The title compound, $(C_5H_{11}OS)[RhCl_4(C_2H_6OS)_2]$, is built up of $[(CH_3)_2SCH_2C(O)CH_3]^+$ cations and $[RhCl_4\{(CH_3)_2SO\}_2]^-$ 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 (dmso-*S*).