References

Ceccio, S. M. (1988). MS thesis, Univ. of California, Los Angeles, USA.
Cheng, B., Safo, M. K., Orosz, R. D., Reed, C. A., Debrunner, P. G. & Scheidt, W. R. (1994). *Inorg. Chem.* **33**, 1319–1324.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Messerschmitt, A. & Pflugrath, J. W. (1987). *J. Appl. Cryst.* **20**, 306–315.
Scheidt, W. R., Cohen, I. A. & Kastner, M. E. (1979). *Biochemistry*, **18**, 3546–3552.
Scheidt, W. R. & Reed, C. A. (1981). *Chem. Rev.* **81**, 543–555.
Scheidt, W. R. & Turowska-Tyrk, I. (1994). *Inorg. Chem.* **33**, 1314–1318.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1995). C**51**, 1275–1278

A Hexacobalt Sulfide Cluster Compound, $[Co_6(\mu\text{-}S)_8(PPh_3)_6].2PPh_3.2C_2H_4Cl_2.H_2O$

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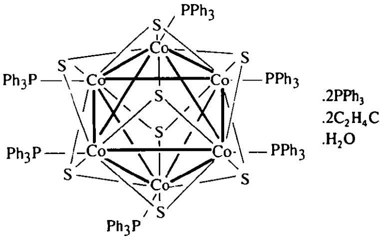
Abstract

The title compound, octa-μ_3-thio-hexakis(triphenylphosphine)-*octahedro*-hexacobalt–triphenylphosphine–1,2-dichloroethane–water (1/2/2/1), $[Co_6S_8(C_{18}H_{15}P)_6]$.-$2C_{18}H_{15}P.2C_2H_4Cl_2.H_2O$, was prepared by the reaction of $CoCl(PPh_3)_3$ with Na(mpo) (mpo = 2-mercaptopyridine *N*-oxide) or NaS^tBu. The molecular structure consists of discrete cluster units interspersed with molecules of free triphenylphosphine and solvent. The neutral cluster contains a slightly distorted Co_6 octahedron with each triangular face symmetrically capped by a μ_3-S ligand. The molecular structure possesses a crystallographic inversion centre. The average Co—Co, Co—S and Co—P bond distances are 2.87 (6), 2.24 (1) and 2.162 (7) Å, respectively. The hexacobalt sulfide cluster compound was formed *via* the capture of S atoms from thiolate reactants.

Comment

The title hexacobalt cluster compound, (I), consists of discrete $[Co_6(\mu_3\text{-}S)_8(PPh_3)_6]$ cluster units interspersed with molecules of free triphenylphosphine, dichloroethane and water. The neutral cluster contains a slightly distorted Co_6 octahedron with each triangular face symmetrically capped by a μ_3-S ligand. The six Co atoms are each terminally coordinated by one triphenylphosphine ligand. Therefore, each Co atom is surrounded by four S atoms and one P atom in a distorted square-pyramidal environment, along with another four Co atoms. The cluster could also be described as a slightly distorted S_8 cube with the Co atoms in face-centred positions. The molecular structure possesses a crystallographic inversion centre within the Co_6 core.



(I)

The mean Co—Co distance in the title complex, 2.87 (6) Å, is longer than in the cation $[Co_6S_8(PPh_3)_6]^+$ (2.81 Å; Fenske, Hachgenei & Ohmer, 1985) or in $[Co_6S_8(PEt_3)_6]$ (2.81 Å; Cecconi, Ghilardi, Midollini & Orlandini, 1983), while the mean Co—S distance [2.24 (1) Å] is similar to that in $[Co_6S_8(PPh_3)_6]^+$ (2.22 Å) and $[Co_6S_8(PEt_3)_6]$ (2.23 Å). It seems that the Co—Co bond lengths are affected by a change in the cluster charge or the phosphine ligands. The Co—S bonds also appear to make an important contribution to the stability of the cluster framework. The Co—Co—Co bond angles fall within the ranges 59.15 (5)–60.56 (5) and 88.87 (6)–91.13 (6)°, and are comparable with the values of 60 and 90° for perfect octahedral symmetry. It is interesting that the uncoordinated triphenylphosphine molecules act as solvate molecules and lie outside the neutral $[Co_6S_8(PPh_3)_6]$ units, as shown in Fig. 2.

The title compound was synthesized *via* a novel route in which the sulfide ligands were obtained indirectly. To date, polynuclear metal sulfides have been prepared by using inorganic sulfur salts as the sulfide source (Fenske, Hachgenei & Ohmer, 1985). Recently, we have found that using Co^{1+} and thiolates or dithiolates leads to the isolation of polycobalt sulfides such as $[Co_4S(SCH_2CH_2S)_3(PPh_3)_3Cl]$ (Jiang, Huang, Wu, Kang, Hong & Liu, 1993) or $[Co_7S_6(PPh_3)_{7-n}X_n]$ (n = 1, 3; X = Br, Cl) (Jiang, Lei, Hong, Huang, Kang & Liu, 1993). These reactions are of particular interest where the sulfide ligands are obtained indirectly. Substitution of mpo^- (2-mercaptopyridine *N*-oxide) or S^tBu for the thiolates leads to the title compound. This reaction also shows that under appropriate conditions (long reaction times, for instance) the S atoms dissociate completely from the thiolates and are incorporated into the

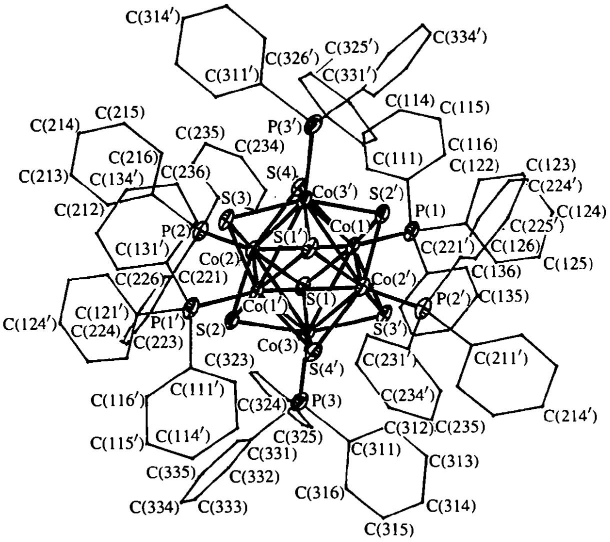


Fig. 1. Molecular structure of the [$Co_6S_8(PPh_3)_6$] cluster showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

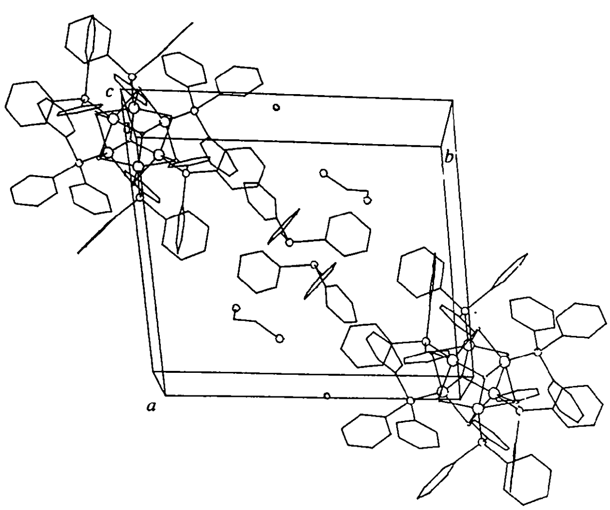


Fig. 2. A view of the packing of the title compound in the unit cell.

cluster without any original thiolate ligands being coordinated. The title compound provides another example of a polycobalt sulfide complex formed *via* the capture of S atoms from organosulfide reactants. The disruption of the C—S bonds found in this reaction system may be related to the mechanism of hydrodesulfurization catalytic processes (Massoth & Kirby, 1977).

Experimental

Crystals of the title compound were obtained from the anaerobic reaction of $CoCl(PPh_3)_3$ with Na(mpo) or NaS^{t}Bu in a 1:2 ratio in the mixed solvent $CH_3OH/C_2H_4Cl_2$ (1:5) for 20 h at room temperature. Recrystallization from warm $C_2H_4Cl_2$ yielded single crystals suitable for X-ray crystallographic analysis.

Crystal data

[$Co_6S_8(C_{18}H_{15}P)_6$].-
$2C_{18}H_{15}P.2C_2H_4Cl_2.H_2O$
$M_r = 2924.34$
Triclinic
$P\bar{1}$
$a = 15.347$ (7) Å
$b = 17.493$ (5) Å
$c = 15.003$ (8) Å
$\alpha = 102.80$ (3)°
$\beta = 116.77$ (3)°
$\gamma = 79.94$ (3)°
$V = 3494$ (3) Å^3
$Z = 1$
$D_x = 1.39$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 6–12°$
$\mu = 1.026$ mm^{-1}
$T = 296$ K
Pyramid
0.5 × 0.4 × 0.4 mm
Black

Data collection

Rigaku MSC/AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.866$, $T_{max} = 1.000$
12793 measured reflections
12280 independent reflections

6624 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.065$
$\theta_{max} = 25°$
$h = 0 \rightarrow 18$
$k = -20 \rightarrow 20$
$l = -17 \rightarrow 15$
3 standard reflections monitored every 250 reflections
intensity decay: 1.2%

Refinement

Refinement on *F*
$R = 0.058$
$wR = 0.069$
$S = 1.40$
6624 reflections
811 parameters
H-atom parameters not refined
Unit weights applied

$(\Delta/\sigma)_{max} = 0.41$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}
Extinction correction: none
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)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co(1)	0.05075 (7)	−0.09951 (6)	−0.06549 (8)	1.77 (4)
Co(2)	0.12968 (7)	0.00054 (6)	0.12862 (8)	1.78 (4)
Co(3)	0.05463 (7)	0.06532 (6)	−0.05566 (8)	1.81 (4)
S(1)	0.1779 (1)	−0.0265 (1)	0.0046 (1)	2.05 (7)
S(2)	0.0996 (1)	0.1243 (1)	0.1024 (1)	2.00 (7)
S(3)	0.0171 (1)	0.0262 (1)	0.1888 (1)	2.04 (8)
S(4)	0.0968 (1)	−0.1251 (1)	0.0914 (2)	2.12 (7)
P(1)	0.0780 (2)	−0.2002 (1)	−0.1655 (2)	2.13 (8)
P(2)	0.2686 (2)	−0.0018 (1)	0.2619 (2)	2.15 (8)
P(3)	0.1175 (2)	0.1463 (1)	−0.0952 (2)	2.30 (8)
C(111)	0.1470 (6)	−0.2882 (5)	−0.1092 (6)	2.7 (3)
C(112)	0.2209 (7)	−0.2774 (5)	−0.0135 (7)	3.5 (4)
C(113)	0.2802 (8)	−0.3417 (6)	0.0313 (8)	5.4 (5)
C(114)	0.2646 (9)	−0.4167 (6)	−0.0224 (9)	5.2 (5)

C(115)	0.1918 (8)	−0.4293 (5)	−0.1173 (8)	4.6 (5)
C(116)	0.1335 (7)	−0.3645 (5)	−0.1622 (7)	3.7 (4)
C(121)	−0.0337 (6)	−0.2387 (5)	−0.2694 (6)	2.7 (3)
C(122)	−0.0842 (7)	−0.2909 (5)	−0.2583 (7)	3.7 (4)
C(123)	−0.1675 (8)	−0.3195 (6)	−0.338 (1)	5.4 (5)
C(124)	−0.2034 (9)	−0.2942 (9)	−0.427 (1)	7.2 (6)
C(125)	−0.159 (1)	−0.2396 (8)	−0.4403 (8)	6.0 (6)
C(126)	−0.0736 (7)	−0.2109 (6)	−0.3619 (8)	4.2 (4)
C(131)	0.1486 (6)	−0.1887 (5)	−0.2335 (6)	2.7 (3)
C(132)	0.1974 (7)	−0.1235 (5)	−0.2090 (6)	3.4 (4)
C(133)	0.2518 (8)	−0.1174 (6)	−0.2610 (8)	4.5 (5)
C(134)	0.2562 (8)	−0.1771 (7)	−0.3360 (8)	4.6 (5)
C(135)	0.2088 (8)	−0.2434 (6)	−0.3598 (7)	4.2 (5)
C(136)	0.1544 (7)	−0.2494 (5)	−0.3090 (7)	3.7 (4)
C(211)	0.2607 (6)	0.0107 (5)	0.3825 (6)	2.5 (3)
C(212)	0.3146 (7)	0.0622 (5)	0.4658 (7)	3.8 (4)
C(213)	0.3120 (8)	0.0661 (6)	0.5581 (7)	4.9 (5)
C(214)	0.2543 (8)	0.0203 (7)	0.5676 (7)	4.9 (5)
C(215)	0.2005 (7)	−0.0303 (7)	0.4835 (8)	4.7 (5)
C(216)	0.2023 (6)	−0.0362 (6)	0.3907 (7)	3.5 (4)
C(221)	0.3535 (6)	0.0719 (5)	0.2888 (6)	2.5 (3)
C(222)	0.3186 (6)	0.1498 (5)	0.2900 (6)	3.1 (3)
C(223)	0.3818 (7)	0.2075 (5)	0.3161 (8)	4.3 (4)
C(224)	0.4794 (8)	0.1872 (6)	0.3412 (9)	4.9 (5)
C(225)	0.5138 (7)	0.1101 (6)	0.3411 (9)	5.0 (5)
C(226)	0.4523 (6)	0.0525 (6)	0.3159 (8)	4.1 (4)
C(231)	0.3511 (6)	−0.0920 (5)	0.2688 (6)	2.6 (3)
C(232)	0.3685 (7)	−0.1258 (5)	0.1862 (7)	3.9 (4)
C(233)	0.4395 (8)	−0.1896 (6)	0.1921 (8)	4.7 (5)
C(234)	0.4919 (8)	−0.2202 (6)	0.280 (1)	4.9 (5)
C(235)	0.4734 (7)	−0.1864 (6)	0.3632 (8)	4.4 (4)
C(236)	0.4035 (7)	−0.1226 (5)	0.3577 (7)	3.9 (4)
C(311)	0.0651 (6)	0.1545 (6)	−0.2293 (6)	3.0 (4)
C(312)	0.0642 (8)	0.0859 (7)	−0.2960 (7)	4.6 (5)
C(313)	0.039 (1)	0.090 (1)	−0.397 (1)	6.8 (7)
C(314)	0.010 (1)	0.163 (1)	−0.428 (1)	8 (1)
C(315)	0.009 (1)	0.229 (1)	−0.364 (1)	8.5 (9)
C(316)	0.0374 (8)	0.2252 (7)	−0.2640 (8)	5.7 (6)
C(321)	0.2487 (6)	0.1239 (5)	−0.0657 (7)	2.7 (3)
C(322)	0.3132 (7)	0.1087 (5)	0.0279 (8)	3.6 (4)
C(323)	0.4116 (7)	0.0927 (6)	0.0522 (8)	4.4 (4)
C(324)	0.4478 (7)	0.0913 (6)	−0.015 (1)	4.9 (5)
C(325)	0.3840 (9)	0.1065 (7)	−0.110 (1)	5.2 (5)
C(326)	0.2845 (7)	0.1243 (6)	−0.1361 (7)	4.1 (4)
C(331)	0.1134 (7)	0.2508 (5)	−0.0366 (7)	2.9 (4)
C(332)	0.1875 (9)	0.2964 (6)	−0.013 (1)	7.2 (6)
C(333)	0.181 (1)	0.3757 (7)	0.024 (1)	9.6 (8)
C(334)	0.101 (1)	0.4094 (6)	0.040 (1)	6.8 (6)
C(335)	0.0285 (8)	0.3655 (6)	0.0192 (8)	4.4 (5)
C(336)	0.0347 (7)	0.2855 (5)	−0.0182 (7)	3.6 (4)
P(01)*	0.4919 (4)	0.4610 (3)	0.7602 (4)	4.2 (2)
P(01′)*	0.3104 (4)	0.5210 (3)	0.6742 (4)	4.2 (2)
C(011)	0.411 (1)	0.430 (1)	0.815 (2)	13 (1)
C(012)	0.427 (1)	0.393 (1)	0.887 (1)	7.9 (7)
C(013)	0.361 (1)	0.346 (1)	0.874 (1)	10 (1)
C(014)	0.279 (1)	0.3384 (9)	0.788 (2)	10 (1)
C(015)	0.264 (1)	0.378 (1)	0.715 (1)	8.9 (9)
C(016)	0.327 (2)	0.429 (2)	0.731 (2)	14 (2)
C(021)	0.436 (1)	0.439 (1)	0.616 (1)	12 (1)
C(022)	0.362 (2)	0.493 (1)	0.579 (1)	10 (1)
C(023)	0.327 (1)	0.5064 (8)	0.484 (1)	7.5 (7)
C(024)	0.362 (1)	0.463 (1)	0.421 (1)	6.7 (8)
C(025)	0.435 (1)	0.4070 (9)	0.453 (1)	7.2 (8)
C(026)	0.472 (1)	0.3935 (8)	0.551 (1)	7.5 (7)
C(031)	0.483 (2)	0.575 (1)	0.786 (2)	17 (1)
C(032)	0.546 (1)	0.629 (2)	0.813 (1)	10 (1)
C(033)	0.529 (2)	0.701 (1)	0.860 (1)	9 (1)
C(034)	0.451 (2)	0.718 (1)	0.874 (1)	8.7 (9)
C(035)	0.384 (1)	0.664 (2)	0.841 (2)	11 (1)
C(036)	0.403 (1)	0.595 (1)	0.795 (2)	18 (1)
Cl(1)	0.7204 (4)	0.2714 (3)	0.5782 (3)	10.7 (3)
Cl(2)*	0.845 (1)	0.4009 (6)	0.7557 (8)	15.3 (7)
Cl(2′)*	0.732 (1)	0.4117 (6)	0.7716 (7)	13.5 (8)
C(41)	0.776 (2)	0.263 (1)	0.707 (1)	11 (1)
C(42)	0.786 (2)	0.326 (2)	0.772 (2)	14 (2)
O(1*W*)*	0.974 (1)	0.458 (1)	0.600 (2)	11 (1)

* Site occupancy factor = 0.5.

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

Co(1)—Co(2)	2.884 (2)	Co(2)—Co(3^{i})	2.884 (2)
Co(1)—Co(2^{i})	2.872 (2)	Co(2)—S(1)	2.228 (2)
Co(1)—Co(3)	2.864 (2)	Co(2)—S(2)	2.219 (2)
Co(1)—Co(3^{i})	2.847 (2)	Co(2)—P(2)	2.170 (3)
Co(1)—S(1)	2.230 (2)	Co(3)—S(1)	2.239 (3)
Co(1)—S(2^{i})	2.217 (2)	Co(3)—S(4^{i})	2.249 (3)
Co(1)—S(3^{i})	2.236 (2)	Co(3)—P(3)	2.157 (2)
Co(1)—S(4)	2.258 (3)	P(1)—C(111)	1.846 (9)
Co(1)—P(1)	2.159 (3)	P(1)—C(121)	1.832 (8)
Co(2)—Co(3)	2.884 (2)	P(1)—C(131)	1.849 (8)
Co(2)—Co(1)—Co(2^{i})	91.13 (6)	S(3^{i})—Co(1)—S(4)	155.24 (9)
Co(2^{i})—Co(1)—Co(3^{i})	60.56 (5)	Co(1)—Co(2)—Co(1^{i})	88.87 (6)
Co(2)—Co(1)—Co(3^{i})	60.43 (5)	Co(1^{i})—Co(2)—Co(3^{i})	59.68 (5)
Co(2^{i})—Co(1)—Co(3)	60.36 (5)	Co(1^{i})—Co(2)—Co(3)	59.28 (5)
Co(2)—Co(1)—Co(3)	60.23 (5)	Co(1)—Co(2)—Co(3^{i})	59.15 (5)
Co(3)—Co(1)—Co(3^{i})	90.24 (5)	Co(1)—Co(2)—Co(3)	59.55 (5)
Co(2)—Co(1)—S(1)	49.66 (7)	Co(3)—Co(2)—Co(3^{i})	89.11 (6)
Co(2)—Co(1)—S(2^{i})	109.56 (8)	Co(1)—Co(2)—S(1)	49.73 (6)
Co(2^{i})—Co(1)—S(2^{i})	49.67 (6)	Co(1)—Co(2)—S(2)	108.00 (8)
Co(2)—Co(1)—S(3^{i})	109.81 (8)	Co(1^{i})—Co(2)—S(2)	49.61 (6)
Co(2^{i})—Co(1)—S(3^{i})	49.79 (6)	Co(1)—Co(2)—P(2)	133.90 (8)
Co(2)—Co(1)—S(4)	49.70 (6)	Co(1)—S(1)—Co(2)	80.61 (8)
Co(2^{i})—Co(1)—S(4)	110.69 (8)	Co(2)—S(1)—Co(3)	80.42 (8)
Co(2^{i})—Co(1)—P(1)	122.08 (8)	Co(3)—S(1)—Co(1)	79.71 (8)
Co(2)—Co(1)—P(1)	146.64 (8)	Co(3)—Co(1)—S(3^{i})	50.07 (6)
Co(3)—Co(1)—S(1)	50.29 (7)	Co(3^{i})—Co(1)—S(3^{i})	109.73 (7)
S(1)—Co(1)—S(2^{i})	154.61 (9)	Co(3)—Co(1)—P(1)	130.95 (7)
S(2^{i})—Co(1)—S(3^{i})	87.37 (9)		

Symmetry code: (i) $-x$, $-y$, $-z$.

Intensity data were corrected for Lorentz–polarization effects and absorption. The structure was solved by direct methods and then by difference Fourier syntheses. All Co, S and P atoms were located from an *E* map. All non-H atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters. H atoms were included in the structure-factor calculations at idealized positions but were not refined. The P atoms of the free triphenylphosphine PPh_3 molecules were statistically distributed with site occupancy factors of 0.5. The atoms Cl(2) and Cl(2′) in the $C_2H_4Cl_2$ solvent molecule were also found to be disordered with site occupancy factors of 0.5. The H_2O solvent molecule site was only half occupied.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *SDP* (Frenz, 1978). Structure solution: *MULTAN*11/82 (Main *et al.*, 1982). Structure refinement: *LSFM* (B. A. Frenz & Associates Inc., 1985). Molecular graphics: *ORTEP*II (Johnson, 1976). Computer: VAX 11/785.

This work was partly supported by a National Natural Science Foundation grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: KH1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

B. A. Frenz & Associates Inc. (1985). *LSFM*. College Station, Texas, USA, and Enraf–Nonius, Delft, The Netherlands.

Cecconi, F., Ghilardi, C. A., Midollini, S. & Orlandini, A. (1983). *Inorg. Chim. Acta*, **76**, L183–L184.

Fenske, D., Hachgenei, J. & Ohmer, J. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 706–709.
Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
Jiang, F.-L., Huang, Z.-Y., Wu, D.-X., Kang, B.-S., Hong, M.-C. & Liu, H.-Q. (1993). *Inorg. Chem.* **32**, 4971–4973.
Jiang, F.-L., Lei, X.-J., Hong, M.-C., Huang, Z.-Y., Kang, B.-S. & Liu, H.-Q. (1993). *J. Organomet. Chem.* **443**, 229–231.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Massoth, F. E. & Kirby, C. L. (1977). *J. Catal.* **47**, 300.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1995). C**51**, 1278–1280

Carbonyl-κ*C*-[tris(diphenylphosphinoyl)methanido-κ²*O*,*O*′][tris(*o*-tolyl)phosphine-κ*P*]rhodium(I), [Rh(C{P(O)Ph₂}₃)(CO){P(*o*-Tol)₃}]

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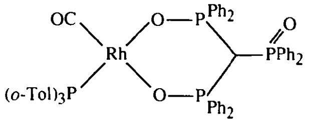
Abstract

The title compound, $[Rh(C_{37}H_{30}P_3O_3)(C_{21}H_{21}P)(CO)]$, has approximate square-planar coordination geometry around the Rh atom. The significant difference [0.012 (3) Å] in the Rh—O bond lengths is due to the slightly different *trans* influence of P(*o*-Tol)₃ and CO. This suggests that the longer Rh—O bond [*trans* to P(*o*-Tol)₃] will be preferentially substituted during intramolecular fluxional coordination behaviour of the tripodal ligand.

Comment

This structure determination forms part of an extension of our studies of square-planar rhodium(I) complexes (Basson, Leipoldt, Roodt & Preston, 1991) of the form $[Rh(L,L')(CO)(PR_3)]$ (where L,L' is a monoanionic bidentate ligand) to include tripodal ligands of the form $[Ph_2P(X)][Ph_2P(Y)][Ph_2P(Z)]CH$ (hereafter HTris*XYZ*, where *X*, *Y* and *Z* are Group VIB elements). Rhodium(I) and iridium(I) complexes containing the $TrisO_3^-$ ligand have been found to be efficient catalysts for the cyclotrimerization and hydrosilylation of acetylenes (Tanke & Crabtree, 1990). Oxidative addition very often forms part of a catalytic cycle and in this context we are studying the mechanisms of oxidative addition of iodomethane to various Rh^I complexes formulated above. Structural results are sometimes of immense value as an aid in formulating the intimate nature of reaction mechanisms (Leipoldt, Basson, Roodt & Purcell, 1992) and the possible *trans* influence of P(*o*-Tol)₃ in the title complex, (I), concerned us in view of its unusual reactivity towards a number of common organic solvents and the known fluxional behaviour between the coordinated and uncoordinated arms in bidentate $TrisS_3^-$ complexes (Browning, Beveridge, Bushnell & Dixon, 1986).



(I)

The Rh atom in (I) displays the usual square-planar geometry with the tripodal ligand coordinated in the bidentate mode *via* two O atoms. The C atom of the carbonyl group is situated 0.343 (4) Å from the plane defined by Rh, O1, O2 and P4. The Rh—P distance of 2.231 (1) Å is within the range 2.232 (2)–2.245 (2) Å

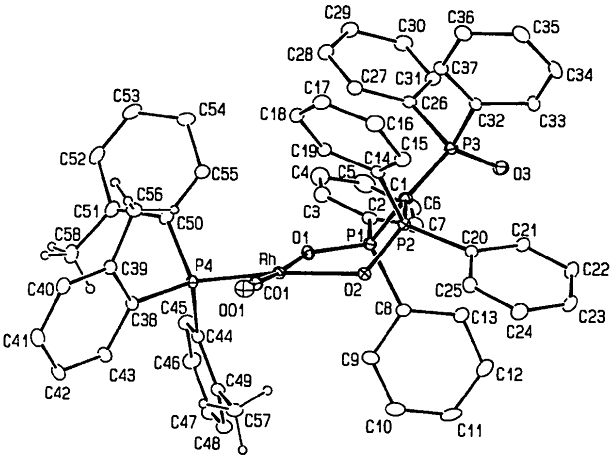


Fig. 1. The molecular structure of the title complex showing 50% probability ellipsoids. Phenyl ring H atoms are omitted for clarity.