Fig. 2. Labelled diagram of [(C₇H₇)₃PC(CH₃)₂CH₂COCH₃]₂- [TcCl₆] (II).

angles [mean 107.8 (2)°]. The average P—C(1)—C angle is 108.7 (3)° while the average P—C—C(tolyl) angle is 120.8 (4)°. As expected the C—C—O angles [122.2 (7) and 123.5 (5)°] are larger than the C(2)—C(3)—C(4) angle [114.3 (5)°]. Also, the angle around C(2) is larger [117.1 (4)°] than the expected tetrahedral value.

References

BANDOLI, G., CLEMENTE, D. A. & MAZZI, U. (1976). *J. Chem. Soc. Dalton Trans.* pp. 125–130.

BANDOLI, G., CLEMENTE, D. A., MAZZI, U. & RONCARI, E. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1381–1384.

CLARKE, M. J. & PODBIELSKI, L. (1987). *Coord. Chem. Rev.* **78**, 253–331.

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MAZZI, U., DE PAOLI, G., DI BERNARDO, P. & MAGON, L. (1976). *J. Inorg. Nucl. Chem.* **38**, 721–725.

MELANSON, R. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 2371–2374.

MELNIK, M. & VAN LIER, J. E. (1987). *Coord. Chem. Rev.* pp. 275–324.

NICOLINI, M., BANDOLI, G. & MAZZI, U. (1990). *Technetium and Rhenium in Chemistry and Nuclear Medicine*. New York: Raven Press.

PEARSTEIN, R. M., DAVIS, W. M., JONES, A. G. & DAVISON, A. (1989). *Inorg. Chem.* **28**, 3332–3334.

ROCHON, F. D., MELANSON, R. & KONG, P. C. (1991a). *Can J. Chem.* **69**, 397–403.

ROCHON, F. D., MELANSON, R. & KONG, P. C. (1991b). *Acta Cryst.* C47, 732–737.

SHELDRICK, G. M. (1984). *SHELXTL User's Manual*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

& van Lier, 1987, and references therein) and other bonds *trans* to a Cl ligand (Bandoli *et al.*, 1982; Rochon *et al.*, 1991*a,b*). The angles around the Tc atoms are close to the octahedral values.

The P—C(tolyl) distances in the cation vary from 1.792 (4) to 1.799 (5) Å, while the P—C(1) distance is significantly longer [1.867 (7) Å], similar to the values observed for [PPh₃{C(CH₃)₂CH₂COCH₃}]- [Tc(PPh₃)Cl₅] where the P—C(phenyl) bond lengths are 1.77 (2), 1.81 (2) and 1.83 (2) Å, and the fourth bond is 1.87 (2) Å (Bandoli *et al.*, 1982). The angles around the P atom are close to the tetrahedral value. The C(1)—P—C(tolyl) angles are slightly larger [mean 111.1 (2)°] than the C(tolyl)—P—C(tolyl)

Structure of μ₆-Carbido-undecacarbonyldi(μ₃-sulfido)(triphenylphosphine)-*triprismo*-hexacobalt

BY GIULIANA GERVASIO AND ROSANNA ROSSETTI

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali dell'Università, Via P. Giuria 7, 10125 Torino, Italy

Abstract. [CoC(S)₂(C₁₈H₁₅P)(CO)₁₁], monoclinic, $P2_1/n$, $M_r = 1000.14$, $a = 8.952$ (1), $b = 15.356$ (2), $c = 26.317$ (3) Å, $\beta = 98.0$ (1)°, $V = 3582.7$ (7) Å³, $Z = 4$, $D_x = 1.854$ Mg m⁻³, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 2.930$ mm⁻¹, $F(000) = 1968$, $T = 293$ K, $R = 0.075$ for 2269 reflections. The compound consists of a trigonal prism of Co atoms with a C atom inserted into the polyhedron. Two S atoms cap the triangular

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co(1)	1044 (3)	2990 (2)	565 (1)	41 (1)
Co(2)	1958 (3)	1488 (2)	607 (1)	43 (1)
Co(3)	2518 (3)	2402 (2)	1382 (1)	31 (1)
Co(4)	3636 (3)	3541 (2)	280 (1)	46 (1)
Co(5)	4491 (3)	2031 (2)	281 (1)	48 (1)
Co(6)	5117 (3)	2925 (2)	1039 (1)	38 (1)
S(1)	220 (6)	1996 (4)	1059 (2)	50 (2)
S(2)	6045 (6)	3167 (4)	319 (2)	54 (2)
P	2336 (5)	3264 (4)	2083 (2)	33 (2)
C(0)	3123 (20)	2584 (15)	717 (7)	42 (7)
C(11)	−72 (27)	2907 (16)	−85 (10)	60 (10)
O(11)	−659 (25)	2905 (15)	−492 (8)	110 (10)
C(12)	205 (26)	4024 (20)	689 (9)	70 (11)
O(12)	−402 (23)	4657 (15)	700 (8)	114 (10)
C(21)	1000 (30)	1071 (16)	0 (9)	64 (10)
O(21)	374 (25)	818 (13)	−360 (8)	104 (10)
C(22)	2633 (28)	449 (20)	839 (10)	67 (11)
O(22)	3075 (29)	−260 (12)	961 (9)	115 (11)
C(31)	3273 (24)	1502 (16)	1762 (8)	43 (8)
O(31)	3778 (21)	890 (12)	1969 (7)	77 (8)
C(41)	2927 (26)	3704 (20)	−396 (10)	74 (12)
O(41)	2632 (28)	3782 (18)	−816 (8)	137 (13)
C(42)	3384 (27)	4632 (19)	467 (10)	63 (10)
O(42)	3266 (26)	5360 (14)	595 (8)	100 (10)
C(51)	5712 (39)	1079 (20)	432 (12)	89 (14)
O(51)	6419 (28)	479 (15)	559 (12)	144 (14)
C(52)	3840 (34)	1738 (23)	−383 (12)	89 (13)
O(52)	3522 (30)	1619 (17)	−796 (8)	126 (12)
C(61)	6274 (24)	2199 (15)	1448 (8)	46 (8)
O(61)	7043 (20)	1673 (13)	1690 (8)	83 (8)
C(62)	5510 (24)	3929 (19)	1387 (11)	62 (10)
O(62)	5731 (21)	4646 (12)	1568 (7)	78 (8)
C(1)	1455 (14)	2670 (9)	2579 (4)	29 (4)
C(2)	1738 (14)	2962 (9)	3085 (4)	54 (6)
C(3)	515 (14)	1955 (9)	2455 (4)	41 (5)
C(4)	−143 (14)	1531 (9)	2837 (4)	57 (6)
C(5)	140 (14)	1823 (9)	3343 (4)	57 (6)
C(6)	1080 (14)	2539 (9)	3467 (4)	61 (6)
C(1')	1222 (12)	4261 (10)	1980 (6)	40 (5)
C(2')	1830 (12)	4965 (10)	1743 (6)	50 (6)
C(3')	1026 (12)	5744 (10)	1670 (6)	71 (7)
C(4')	−384 (12)	5819 (10)	1834 (6)	68 (7)
C(5')	−991 (12)	5115 (10)	2071 (6)	59 (6)
C(6')	−188 (12)	4336 (10)	2144 (6)	58 (6)
C(1")	4131 (13)	3639 (8)	2463 (5)	32 (5)
C(2")	4227 (13)	4451 (8)	2703 (5)	53 (6)
C(3")	5539 (13)	4689 (8)	3023 (5)	51 (6)
C(4")	6754 (13)	4113 (8)	3104 (5)	57 (6)
C(5")	6658 (13)	3300 (8)	2865 (5)	58 (6)
C(6")	5347 (13)	3063 (8)	2544 (5)	34 (5)

Table 2. Bond lengths (Å) and angles (°)

Co(1)—Co(2)	2.445 (4)	Co(1)—Co(3)	2.528 (4)
Co(1)—Co(4)	2.674 (4)	Co(1)—S(1)	2.197 (7)
Co(1)—C(0)	1.950 (18)	Co(1)—C(11)	1.863 (24)
Co(1)—C(12)	1.805 (30)	Co(2)—Co(3)	2.470 (4)
Co(2)—Co(5)	2.667 (4)	Co(2)—S(1)	2.227 (7)
Co(2)—C(0)	1.981 (22)	Co(2)—C(21)	1.819 (24)
Co(2)—C(22)	1.783 (30)	Co(3)—Co(6)	2.731 (4)
Co(3)—S(1)	2.204 (6)	Co(3)—P	2.294 (6)
Co(3)—C(0)	1.924 (20)	Co(3)—C(31)	1.782 (22)
Co(4)—Co(5)	2.441 (4)	Co(4)—Co(6)	2.431 (4)
Co(4)—S(2)	2.220 (6)	Co(4)—C(0)	1.960 (22)
Co(4)—C(41)	1.819 (27)	Co(4)—C(42)	1.769 (29)
Co(5)—Co(6)	2.422 (4)	Co(5)—S(2)	2.225 (7)
Co(5)—C(0)	1.982 (20)	Co(5)—C(51)	1.836 (32)
Co(5)—C(52)	1.819 (31)	Co(6)—S(2)	2.203 (7)
Co(6)—C(0)	1.938 (18)	Co(6)—C(61)	1.778 (21)
Co(6)—C(62)	1.804 (28)	P—C(1)	1.855 (13)
P—C(1')	1.827 (15)	P—C(1")	1.862 (12)
C(11)—O(11)	1.125 (31)	C(12)—O(12)	1.117 (37)
C(21)—O(21)	1.104 (31)	C(22)—O(22)	1.188 (36)
C(31)—O(31)	1.147 (29)	C(41)—O(41)	1.108 (34)
C(42)—O(42)	1.176 (36)	C(51)—O(51)	1.142 (40)
C(52)—O(52)	1.101 (37)	C(61)—O(61)	1.188 (28)
C(62)—O(62)	1.205 (34)		
Co(2)—Co(1)—Co(3)	59.6 (1)	Co(2)—Co(1)—Co(4)	90.8 (1)
Co(3)—Co(1)—Co(4)	88.9 (1)	Co(2)—Co(1)—S(1)	57.0 (2)
Co(3)—Co(1)—S(1)	55.1 (2)	Co(4)—Co(1)—S(1)	139.6 (2)
Co(2)—Co(1)—C(11)	96.3 (7)	Co(3)—Co(1)—C(11)	155.1 (8)
Co(4)—Co(1)—C(11)	98.0 (8)	S(1)—Co(1)—C(11)	108.3 (8)
Co(2)—Co(1)—C(12)	165.2 (8)	Co(3)—Co(1)—C(12)	110.0 (7)
Co(4)—Co(1)—C(12)	99.8 (8)	S(1)—Co(1)—C(12)	108.8 (9)
C(11)—Co(1)—C(12)	92.4 (10)	Co(1)—Co(2)—Co(3)	61.9 (1)
Co(1)—Co(2)—Co(5)	89.1 (1)	Co(3)—Co(2)—Co(5)	90.2 (1)
Co(1)—Co(2)—S(1)	55.9 (2)	Co(3)—Co(2)—S(1)	55.7 (2)
Co(5)—Co(2)—S(1)	138.6 (2)	Co(1)—Co(2)—C(21)	100.3 (8)
Co(3)—Co(2)—C(21)	160.3 (8)	Co(5)—Co(2)—C(21)	98.4 (9)
S(1)—Co(2)—C(21)	108.2 (9)	Co(1)—Co(2)—C(22)	162.7 (9)
Co(3)—Co(2)—C(22)	101.8 (8)	Co(5)—Co(2)—C(22)	97.3 (9)
S(1)—Co(2)—C(22)	111.0 (9)	C(21)—Co(2)—C(22)	94.7 (11)
Co(1)—Co(3)—Co(2)	58.6 (1)	Co(1)—Co(3)—Co(6)	88.9 (1)
Co(2)—Co(3)—Co(6)	88.8 (1)	Co(1)—Co(3)—S(1)	54.8 (2)
Co(2)—Co(3)—S(1)	56.6 (2)	Co(6)—Co(3)—S(1)	138.4 (2)
Co(1)—Co(3)—P	113.0 (2)	Co(2)—Co(3)—P	164.4 (2)
Co(6)—Co(3)—P	104.8 (2)	S(1)—Co(3)—P	107.9 (2)
Co(1)—Co(3)—C(31)	150.0 (7)	Co(2)—Co(3)—C(31)	92.3 (7)
Co(6)—Co(3)—C(31)	98.0 (7)	S(1)—Co(3)—C(31)	104.9 (7)
P—Co(3)—C(31)	93.5 (7)	C(0)—Co(3)—C(31)	119.4 (10)
Co(1)—Co(4)—Co(5)	89.0 (1)	Co(1)—Co(4)—Co(6)	92.3 (1)
Co(5)—Co(4)—Co(6)	59.6 (1)	Co(1)—Co(4)—S(2)	141.3 (2)
Co(5)—Co(4)—S(2)	56.8 (2)	Co(6)—Co(4)—S(2)	56.3 (2)
Co(1)—Co(4)—C(41)	96.9 (8)	Co(5)—Co(4)—C(41)	101.4 (10)
Co(6)—Co(4)—C(41)	158.9 (9)	S(2)—Co(4)—C(41)	106.6 (8)
C(0)—Co(4)—C(41)	126.7 (11)	Co(1)—Co(4)—C(42)	94.1 (8)
Co(5)—Co(4)—C(42)	161.9 (8)	Co(6)—Co(4)—C(42)	102.5 (8)
S(2)—Co(4)—C(42)	113.1 (8)	C(41)—Co(4)—C(42)	95.9 (13)
Co(2)—Co(5)—Co(4)	91.0 (1)	Co(2)—Co(5)—Co(6)	91.3 (1)
Co(4)—Co(5)—Co(6)	60.0 (1)	Co(2)—Co(5)—S(2)	141.7 (2)
Co(4)—Co(5)—S(2)	56.6 (2)	Co(6)—Co(5)—S(2)	56.4 (2)
Co(2)—Co(5)—C(51)	100.8 (11)	Co(4)—Co(5)—C(51)	159.0 (10)
Co(6)—Co(5)—C(51)	102.1 (10)	S(2)—Co(5)—C(51)	105.4 (11)
Co(2)—Co(5)—C(52)	93.3 (10)	Co(4)—Co(5)—C(52)	100.1 (11)
Co(6)—Co(5)—C(52)	159.7 (11)	S(2)—Co(5)—C(52)	110.7 (11)
C(51)—Co(5)—C(52)	96.5 (14)	Co(3)—Co(6)—Co(4)	89.7 (1)
Co(3)—Co(6)—Co(5)	89.8 (1)	Co(4)—Co(6)—Co(5)	60.4 (1)
Co(3)—Co(6)—S(2)	140.8 (2)	Co(4)—Co(6)—S(2)	57.0 (2)
Co(5)—Co(6)—S(2)	57.3 (2)	Co(3)—Co(6)—C(61)	93.8 (7)
Co(4)—Co(6)—C(61)	161.2 (7)	Co(5)—Co(6)—C(61)	101.1 (7)
S(2)—Co(6)—C(61)	111.6 (8)	C(0)—Co(6)—C(61)	121.3 (10)
Co(3)—Co(6)—C(62)	101.5 (8)	Co(4)—Co(6)—C(62)	97.4 (8)
Co(5)—Co(6)—C(62)	155.4 (9)	S(2)—Co(6)—C(62)	102.8 (9)
C(0)—Co(6)—C(62)	123.8 (10)	C(61)—Co(6)—C(62)	100.0 (11)
Co(1)—S(1)—Co(2)	67.1 (2)	Co(1)—S(1)—Co(3)	70.1 (2)
Co(2)—S(1)—Co(3)	67.8 (2)	Co(4)—S(2)—Co(5)	66.6 (2)
Co(4)—S(2)—Co(6)	66.7 (2)	Co(5)—S(2)—Co(6)	66.3 (2)
Co(3)—P—C(1)	111.5 (5)	Co(3)—P—C(1')	117.5 (5)
C(1)—p—C(1')	103.9 (6)	Co(3)—P—C(1")	117.3 (5)
C(1)—P—C(1")	101.1 (6)	C(1')—P—C(1")	103.5 (6)
Co(1)—C(11)—O(11)	174.0 (24)	Co(1)—C(12)—O(12)	170.9 (21)
Co(2)—C(21)—O(21)	177.6 (26)	Co(2)—C(22)—O(22)	175.7 (24)
Co(3)—C(31)—O(31)	174.4 (20)	Co(4)—C(41)—O(41)	173.2 (24)
Co(4)—C(42)—O(42)	177.9 (24)	Co(5)—C(51)—O(51)	174.8 (31)
Co(5)—C(52)—O(52)	173.8 (34)	Co(6)—C(61)—O(61)	175.1 (20)
Co(6)—C(62)—O(62)	172.8 (23)		

faces of the prism; five Co atoms link to two carbonyl groups each and one Co atom links to one carbonyl and one triphenylphosphine ligand.

Introduction. Comparing complexes containing the $Co_3(\mu_3\text{-S})$ moiety with those having a $Co_3(\mu_3\text{-}CR)$ (R = alkyl) fragment it was observed that the substitution of a CO group by a $P(C_6H_5)_3$ group caused a great deformation of the metal cluster in chalcogenic compounds (Brice, Penfold, Robinson & Taylor 1970; Markó, Gervasio, Stanghellini & Bor 1985). To verify this feature we began with the determination of the structure of a monosubstituted prismatic $Co_6(\mu_3\text{-S})_2$ cluster.

Experimental. The complex was prepared by the reaction of $Co_6C(CO)_{12}(\mu_3\text{-S})_2$ (0.52 mmol) with $P(C_6H_5)_3$ (0.52 mmol) in anhydrous tetrahydrofuran

(100 ml) stirring the solution under N_2 for 30 min at room temperature. The solvent was removed under vacuum and the residue chromatographed on a silica gel column with petroleum ether as eluent; brown fraction containing the complex was collected, concentrated and cooled at 253 K; crystals of poor quality were obtained.

A brown lamellar crystal ($0.5 \times 0.4 \times 0.2$ mm) was measured on a Nicolet $R3$ diffractometer; cell constants obtained from a least-squares fit to the setting angles of 25 randomly selected reflections in the 2θ range 25–35°; empirical absorption correction applied (transmission coefficient 0.98–0.49) (North, Phillips & Mathews 1968); data collected using the $\omega/2\theta$ scanning procedure with a scan range of 2.0° in ω, variable speed (2–15° min^{-1}), background measured with stationary crystal and stationary counter at beginning and end of scan, each for 30% of total scan time, 2θ range 2–50°, $-10 \le h \le 10$, $0 \le k \le 18$, $0 \le l \le 31$; two standard reflections showed no variation, 6790 reflections collected, 6304 unique reflections ($R_{int} = 0.06$), 2269 observed reflections with $F > 6.0\sigma(F)$; solution by direct methods using the 6304 unique $F_o{}^2$, quantity minimized $\sum w(F_o - F_c)^2$ with full-matrix least squares; $SHELX76$ as source of atomic scattering factors and f', f'' values; 330 refined parameters with anisotropic refinement for Co, S, P, C(0), C_{CO}, O_{CO}, with phenyl rings refined

isotropically as rigid groups. Final $R = 0.075$, $wR = 0.077$, $S = 0.90$, with $w^{-1} = \sigma^2(F) + 0.010F^2$, largest difference peak and hole 1.02 and -0.95 e Å^{-3}, max. $\Delta/\sigma = 0.20$, $SHELX76$ program package (Sheldrick, 1976). Table 1* lists the final atomic fractional coordinates and the equivalent isotropic thermal parameters. Interatomic distances and angles are given in Table 2.

Discussion. The $Co_6C(CO)_{11}[P(C_6H_5)_3]S_2$ compound (Fig. 1) is formed by a prism of Co atoms with the triangular faces capped by μ_3-S atoms and with a C atom inserted in the prism. Five Co atoms link two terminal carbonyl groups and one Co atom links one terminal CO and one $P(C_6H_5)_3$ ligand. The substitution of a CO group by $P(C_6H_5)_3$ in the parent compound $Co_6C(CO)_{12}S_2$ (Bor, Dietler, Stanghellini, Gervasio, Rossetti, Sbrignadello & Battiston, 1981) is followed by a deformation of the prism, involving the Co(1)—Co(3) and the Co(3)—Co(6) bonds cis to $P(C_6H_5)_3$ and, to a lesser extent, the Co(2)—Co(3) bond trans to $P(C_6H_5)_3$ (Table 2). Also in the compound $Co_3(CO)_6[P(C_6H_5)_3]S(SCOMe)$, the same significant effect was seen on the cis Co—Co bonds, due principally to the hindrance of the phenyl groups. The cavity where the C(0) atom is located has a radius of 0.73 Å, in agreement with other similar compounds. The crystal packing shows a short contact (2.57 Å) between an H atom of a phenyl ring and an O atom of a different molecule.
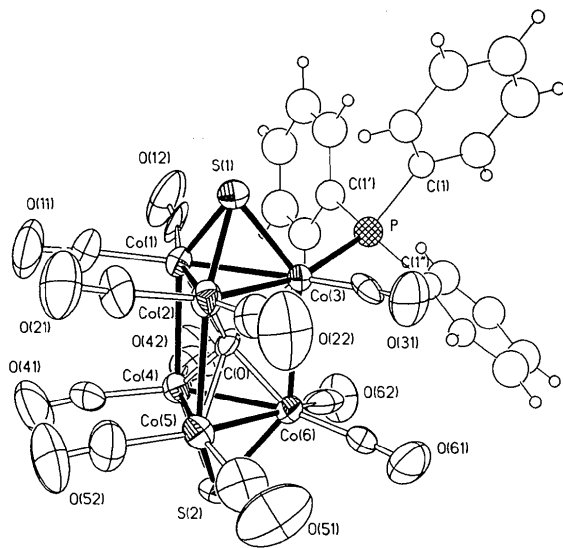

Fig. 1. ORTEP (Johnson, 1965) view of the title cluster. Thermal ellipsoids are drawn at the 50% probability level.

References

Bor, G., Dietler, U. K., Stanghellini, P. L., Gervasio, G., Rossetti, R., Sbrignadello, G. & Battiston, G. A. (1981). *J. Organomet. Chem.* **213**, 277–292.

Brice, M. D., Penfold, B. R., Robinson, W. T. & Taylor, S. R. (1970). *Inorg. Chem.* **9**, 362–367.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Markó, L., Gervasio, G., Stanghellini, P. L. & Bor, G. (1985). *Transition Met. Chem.* **10**, 344–348.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.