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Structures of *trans*-$[TcCl_4\{P(CH_3)_3\}_2]$ and $[P(C_7H_7)_3\{C(CH_3)_2CH_2COCH_3\}]_2[TcCl_6]$

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Abstract. Tetrachlorobis(trimethylphosphine)technetium, *trans*-$[TcCl_4(C_3H_9P)_2]$ (I), $M_r = 392.88$, monoclinic, $P2_1/c$, $a = 6.639$ (2), $b = 8.443$ (3), $c = 13.559$ (4) Å, $\beta = 100.73$ (2)°, $V = 746.7$ (4) Å^3, $Z = 2$, $D_x = 1.738$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.82$ mm^{-1}, $F(000) = 390$, $T = 295$ and $R = 0.036$ for 932 observed reflections. The Tc atom is located on an inversion centre. The Tc—P distances are 2.524 (2) Å while the Tc—Cl bonds are 2.320 (1) and 2.330 (2) Å. Bis[(1,1-dimethyl-3-oxobutyl)tris(4-methylphenyl)phosphonium] hexachlorotechnetate, $[P(C_7H_7)_3(C_6H_{11}O)][TcCl_6]$ (II), $M_r = 1118.68$, monoclinic, $P2_1/c$, $a = 15.120$ (4), $b = 11.038$ (3), $c = 21.146$ (6) Å, $\beta = 128.59$ (2)°, $V = 2759$ (1) Å^3, $Z = 2$, $D_x = 1.344$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.64$ mm^{-1}, $F(000) = 1158$, $T = 295$ K and $R = 0.041$ for 3019 observed reflections. The Tc atom of the $[TcCl_6]^{2-}$ anion is located on an inversion center. The Tc—Cl bonds vary from 2.352 (2) to 2.359 (1) Å. The $[(C_7H_7)_3PC(CH_3)_2CH_2COCH_3]^+$ cation was formed from the reaction of P(p-tolyl)$_3$ with acetone as solvent.

Introduction. The chemistry of technetium has recently become very important especially in relation to the use of the isotope 99*m* in radiopharmacy. ^{99m}Tc is an ideal nucleus for diagnostic studies in nuclear medicine. It has been used for several years for bone scanning and recently it has been used to study the heart, brain, kidneys, liver and other organs, and also tumor tissue. A good review on medical diagnostic imaging with complexes of ^{99m}Tc has been published by Clarke & Podbielski (1987). The most recent advances in this area were published in a book edited by Nicolini, Bandoli & Mazzi (1990).

We have begun a project on the synthesis of new technetium compounds, especially mixed ligand complexes, and have prepared several phosphine compounds as starting materials for these syntheses. Since small quantities of reactants are used, X-ray diffraction is an excellent method for characterizing the Tc compounds when adequate crystals can be prepared. We have now studied the crystal structure of two Tc^{IV} complexes which are reported below. These compounds are *trans*-$[Tc\{P(CH_3)_3\}_2Cl_4]$ and the ionic complex $[(p\text{-tolyl})_3PC(CH_3)_2CH_2COCH_3]_2$-$[TcCl_6]$.

Experimental. Ammonium pertechnetate (NH_4-$^{99}TcO_4$) was purchased from Oak Ridge National Laboratory, recrystallized in nitric acid (caution: ammonium pertechnetate in acid medium will produce some volatile radioactive compounds) and dissolved in water. A 0.286 *M* solution was prepared. All manipulations were made in a laboratory approved for low-level radioactive material (^{99}Tc is a β-emitter with a particle energy of 0.292 MeV and a half-life of 2.13×10^5 years). Trimethylphosphine (1 *M* in toluene) and tri(p-tolyl)phosphine were purchased from Aldrich.

Compound (I) was prepared by a method similar to the one described by Mazzi, de Paoli, di Bernardo & Magon (1976). 2 ml of ammonium pertechnate (0.286 *M*) were added to a solution containing 2 ml of conc. HCl and 15 ml of ethanol. The solution turned yellow immediately. Trimethylphosphine (4 ml, 1 *M* in toluene) was added and the mixture stirred overnight at room temperature, concentrated to about 5 ml and the green precipitate collected by filtration. The compound was air-dried, washed several times with water and the crystals dried in a desiccator over $CaCl_2$. The compound was then recrystallized from tetrachloromethane and green crystals suitable for diffraction methods were obtained. Yield: ~45%. IR (cm^{-1}): 1410, 1288, 1282, 948, 857, 848, 747, 725, 670, 349, 335.

Compound (II) was prepared by adding 1 ml of ammonium pertechnetate (0.286 *M*) to a solution containing 1.5 ml of conc. HCl and 15 ml of ethanol. Tri(p-tolyl)phosphine (0.4 g) was added and the mixture stirred overnight at room temperature, filtered and the remaining orange-red filtrate evaporated to dryness. The yellow residue was dissolved in acetone

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and the resulting mixture was filtered. The precipitate was dissolved in dimethylformamide (DMF) and the solution left to evaporate slowly at room temperature. After several days, crystals suitable for X-ray diffraction were isolated.

The two crystals of (I) and (II) were selected after examination for homogeneity under a polarizing microscope. The unit-cell parameters were obtained by least-squares refinement of the angles 2θ, ω and χ for 15 well centered reflections (15–26°) on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Crystal data and experimental details are summarized in Table 1. Other information is given in Melanson & Rochon (1975). Corrections were made for Lorentz–polarization effects and the anomalous-dispersion terms of Tc, P and Cl were included in the calculations (Cromer, 1974).

The Patterson map showed the position of the Tc atom; other non-H atoms were located by structure-factor and Fourier-map calculations; coordinates and isotropic thermal factors of H atoms were fixed at calculated positions with C—H = 0.96 Å and isotropic thermal factors fixed at 1.2 times the equivalent isotropic U of the C atom to which it is bonded. Individual weights $w = [\sigma^2(F) + 0.0001F^2]^{-1}$ were applied. The refinement (on F) of the scale factor, coordinates and anisotropic temperature factors of all the non-H atoms converged to $R = 0.036$ and $wR = 0.034$ for (I), and to $R = 0.041$ and $wR = 0.041$ for (II). There were a few residual peaks in the environment of the Tc atom.

Scattering curves from *International Tables for X-ray Crystallography* (1974, Vol. IV) were used. The calculations were performed on a Nicolet *SHELXTL* system (Sheldrick, 1984).

Discussion. The reactions of NH_4TcO_4 with PR_3 in ethanol in the presence of HCl have been studied by Mazzi *et al.* (1976). In a 1:5 ratio, the green disubstituted Tc^{IV} compounds, $Tc(PR_3)_2Cl_4$, were prepared with dimethyl(phenyl)phosphine, diethyl(phenyl)-phosphine and triphenylphosphine, while using a 1:15 ratio, the yellow-orange trisubstituted Tc^{III} complexes, $Tc(PR_3)_3Cl_3$ were synthesized with ligands less bulky than PPh_3. With PPh_3, *mer*-$TcCl_3(PPh_3)_2(DMF)$ was isolated in DMF solution (Rochon, Melanson & Kong, 1991*a*). In these reactions, PR_3 acts as the reducing agent. We have observed similar results with methyl(diphenyl)phosphine (Rochon, Melanson & Kong, 1991*b*), but with less bulky phosphines, the reactions are slightly different. With PEt_3, two compounds were obtained and characterized, *trans*-$Tc(PEt_2)_2Cl_4$ and $[PHEt_3][TcCl_5(PEt_3)]$ (Rochon *et al.*, 1991*b*). No trisubstituted compound was detected. We have also studied the reaction of NH_4TcO_4 with trimethylphosphine and tri(*p*-tolyl)phosphine.

Table 1. *Experimental details of the X-ray studies of compounds* (I) *and* (II)

	(I)	(II)
Crystal size (mm)	0.22 × 0.17 × 0.40	0.298 × 0.375 × 0.096
$2\theta_{max}$ (°)	52	52
Quadrants	$h, k, \pm l$	$h, k, \pm l$
h, k, l range	0→8, 0→10, −16→16	0→18, 0→13, −26→20
Scan technique	$2\theta/\theta$	$2\theta/\theta$
Scan rate (° min^{-1})	2.0–24	3.0–24
Standard reflections (variation)	$42\bar{2}$, 204, 042 (<2%)	$34\bar{5}$, 611, 150 (<3%)
No. of independent reflections	1726	5993
No. of observed reflections, criterion	932, $I_{net} > 2.5\sigma$	3019, $I_{net} > 2.7\sigma$
Max. shift/e.s.d.	0.01	0.03
ρ_{max}, ρ_{min} (e Å^{-3})	0.56, −0.48	0.44, −0.34
R	0.036	0.041
wR	0.034	0.041
Standard deviation (unit weight)	1.55	1.15
T (K)	295	295

As expected, compound (I) is the *trans* isomer with the Tc atom on an inversion center. The refined atomic parameters of the structure are listed in Table 2.* A labelled diagram of the molecule is shown in Fig. 1. The bond distances and angles are shown in Table 3.

The Tc—Cl distances are 2.320 (1) and 2.330 (2) Å, very close to the values observed in the literature for *trans* Tc—Cl bonds (Pearstein, Davis, Jones & Davison, 1989; Rochon, Melanson & Kong, 1991*a*; Bandoli, Clemente & Mazzi, 1976; Rochon, Melanson & Kong, 1991*b*). The Tc—P distances of 2.524 (2) Å is slightly shorter than the distances observed for the two Tc^{IV} complexes, *trans*-$Tc^{IV}(PEt_3)_2Cl_4$ [2.541 (1) Å] and *trans*-$Tc^{IV}(PMePh_2)_2Cl_4$ [2.556 (1) Å] (Rochon *et al.*, 1991*b*), and very similar to the value observed for the Tc^{III} compound $TcCl_3(PPh_3)_2(CO)$ [2.525 (2) Å; Pearstein *et al.* (1989)]. It is longer than the distances observed for the Tc—P bonds *trans* to each other in *mer*-$Tc^{III}(Me_2Ph)_3Cl_3$ [2.46 (1)–2.48 (1) Å; Bandoli *et al.* (1976)] and in *mer*-$Tc^{III}(PPh_3)_2Cl_3(DMF)$ [2.496 (5) and 2.499 (5) Å; Rochon *et al.* (1991*a*)]. The longer values for the Tc^{IV} complexes compared to the Tc^{III} compounds might be caused by the greater number of unpaired electrons associated with Tc^{IV} compounds.

The angles around Tc are close to the expected octahedral values. The P—C distances are normal and vary from 1.801 (6) to 1.815 (6) Å while the angles around the P atoms are close to the tetrahedral value. The Tc—P—C angles are slightly larger [111.9 (2)–114.7 (2)°] than the C—P—C values [104.7 (3)—106.1 (3)°] as observed in *trans*-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and stereoscopic views of both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71032 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1023]

Table 2. *Positional parameters* ($\times 10^4$) *with their e.s.d.'s and temperature factors* [$\times 10^4$, $\times 10^3$ *for* O *and* C *of* (II)]

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

	x	y	z	U_{eq} (Å^2)
Compound (I)				
Tc	0	0	0	284 (2)
Cl(1)	2442 (2)	4 (3)	−1021 (1)	482 (4)
Cl(2)	−1793 (3)	1992 (2)	−983 (1)	463 (4)
P	1853 (3)	2167 (2)	1090 (1)	344 (5)
C(1)	3601 (8)	3282 (7)	492 (4)	540 (8)
C(2)	3325 (8)	1496 (7)	2279 (4)	529 (8)
C(3)	91 (8)	3632 (6)	1421 (4)	496 (8)
Compound (II)				
Tc	0	0	0	359 (3)
Cl(1)	30 (1)	271 (1)	−1090 (1)	568 (8)
Cl(2)	576 (1)	2027 (1)	399 (1)	605 (9)
Cl(3)	1903 (1)	−644 (1)	829 (1)	562 (8)
P	3804 (1)	5128 (1)	906 (1)	371 (6)
O	2364 (3)	5375 (4)	2346 (2)	74 (2)
C(1)	3460 (4)	5303 (4)	1609 (3)	41 (3)
C(2)	2178 (4)	5134 (5)	1143 (3)	53 (3)
C(3)	1750 (4)	5259 (4)	1619 (3)	53 (3)
C(4)	488 (4)	5221 (5)	1115 (3)	70 (4)
C(5)	3855 (4)	6561 (5)	2001 (3)	54 (3)
C(6)	4114 (4)	4308 (5)	2269 (3)	60 (4)
C(11)	3907 (4)	3555 (4)	744 (3)	40 (3)
C(12)	4921 (4)	3028 (4)	1011 (3)	43 (3)
C(13)	4962 (4)	1809 (4)	887 (3)	54 (3)
C(14)	4018 (5)	1089 (4)	498 (3)	55 (4)
C(15)	3008 (5)	1609 (5)	226 (3)	61 (4)
C(16)	2941 (4)	2825 (4)	346 (3)	55 (4)
C(17)	4071 (6)	−243 (4)	365 (3)	83 (5)
C(21)	5131 (4)	5862 (4)	1330 (3)	39 (3)
C(22)	5197 (4)	6697 (4)	872 (3)	45 (3)
C(23)	6201 (4)	7251 (4)	1175 (3)	53 (3)
C(24)	7180 (4)	7014 (5)	1950 (3)	51 (3)
C(25)	7111 (4)	6182 (5)	2406 (3)	58 (3)
C(26)	6115 (4)	5609 (5)	2103 (3)	53 (3)
C(27)	8282 (5)	7602 (6)	2277 (4)	82 (4)
C(31)	2772 (4)	5799 (4)	−68 (3)	36 (3)
C(32)	2249 (4)	6898 (4)	−165 (3)	46 (3)
C(33)	1623 (4)	7486 (4)	−902 (3)	52 (3)
C(34)	1515 (4)	7029 (5)	−1554 (3)	47 (3)
C(35)	2002 (4)	5917 (5)	−1467 (3)	57 (3)
C(36)	2618 (4)	5304 (4)	−736 (3)	51 (3)
C(37)	916 (5)	7728 (6)	−2333 (3)	76 (4)

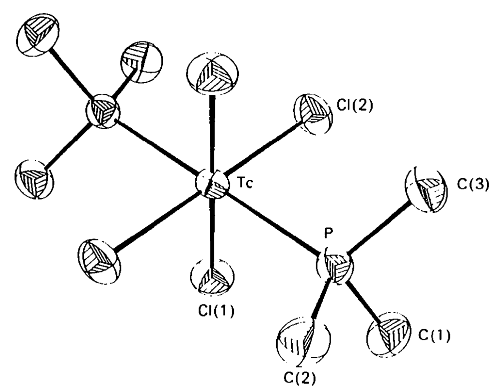

Fig. 1. Labelled diagram of *trans*-[Tc{P(CH$_3$)$_3$}$_2$Cl$_4$] (I).

[Tc(PEt$_3$)$_2$Cl$_4$], *trans*-[Tc(PMePh$_2$)$_2$Cl$_4$] (Rochon *et al.*, 1991*b*), [Tc{P(CH$_3$)$_2$C$_6$H$_5$}$_3$Cl$_3$] (Bandoli *et al.*, 1976) and in [Tc{P(C$_6$H$_5$)}Cl$_5$]$^-$ (Bandoli, Clemente, Mazzi & Roncari, 1982; Rochon *et al.*, 1991*b*).

Compound (II) was prepared by the reaction of P(*p*-tolyl)$_3$ with ammonium pertechnetate in acidic

Table 3. *Bond distances* (Å) *and angles* (°)

Compound (I)			
Tc—Cl(1)	2.320 (1)	P—C(1)	1.801 (6)
Tc—Cl(2)	2.330 (2)	P—C(2)	1.813 (5)
Tc—P	2.524 (2)	P—C(3)	1.815 (6)
Cl(1)—Tc—Cl(2)	89.8 (1)	C(1)—P—C(3)	104.7 (3)
Tc—P—C(1)	113.6 (2)	Cl(2)—Tc—P	87.3 (1)
C(1)—P—C(2)	106.1 (3)	Tc—P—C(3)	111.9 (2)
Cl(1)—Tc—P	91.7 (1)	C(2)—P—C(3)	105.0 (3)
Tc—P—C(2)	114.7 (2)		
Compound (II)			
Tc—Cl(1)	2.352 (2)	C(13)—C(14)	1.371 (8)
P—C(1)	1.867 (7)	C(14)—C(17)	1.508 (7)
P—C(31)	1.792 (4)	C(22)—C(23)	1.370 (8)
C(1)—C(6)	1.552 (7)	C(25)—C(26)	1.369 (8)
C(3)—C(4)	1.498 (8)	C(31)—C(36)	1.394 (9)
C(12)—C(13)	1.379 (7)	C(34)—C(35)	1.384 (8)
C(15)—C(16)	1.382 (7)	Tc—Cl(3)	2.359 (1)
C(21)—C(26)	1.389 (5)	P—C(21)	1.799 (5)
C(24)—C(25)	1.381 (10)	C(1)—C(5)	1.534 (6)
C(31)—C(32)	1.391 (7)	C(3)—O	1.209 (6)
C(33)—C(34)	1.379 (9)	C(11)—C(16)	1.399 (7)
C(34)—C(37)	1.506 (8)	C(14)—C(15)	1.378 (9)
Tc—Cl(2)	2.358 (1)	C(21)—C(22)	1.385 (8)
P—C(11)	1.795 (5)	C(23)—C(24)	1.386 (6)
C(1)—C(2)	1.543 (7)	C(24)—C(27)	1.497 (9)
C(2)—C(3)	1.503 (11)	C(32)—C(33)	1.381 (7)
C(11)—C(12)	1.388 (8)	C(35)—C(36)	1.385 (7)
Cl(1)—Tc—Cl(2)	90.1 (1)	C(11)—C(12)—C(13)	120.1 (5)
C(1)—P—C(11)	110.6 (3)	C(14)—C(15)—C(16)	121.2 (5)
C(11)—P—C(21)	109.2 (2)	C(15)—C(14)—C(17)	120.1 (5)
P—C(1)—C(2)	110.0 (3)	C(22)—C(23)—C(24)	121.5 (6)
P—C(11)—C(12)	122.2 (3)	C(21)—C(26)—C(25)	121.1 (6)
P—C(21)—C(26)	122.7 (5)	C(22)—C(21)—C(26)	117.7 (5)
C(1)—C(2)—C(3)	117.1 (4)	C(33)—C(34)—C(35)	118.1 (5)
C(5)—C(1)—C(6)	109.9 (3)	C(33)—C(34)—C(37)	121.4 (5)
C(4)—C(3)—O	122.2 (7)	Cl(2)—Tc—Cl(3)	90.7 (1)
C(13)—C(14)—C(15)	118.4 (5)	C(1)—P—C(31)	113.3 (2)
C(13)—C(14)—C(17)	121.4 (6)	C(21)—P—C(31)	106.8 (2)
C(21)—C(22)—C(23)	120.8 (4)	P—C(1)—C(6)	107.8 (4)
C(24)—C(25)—C(26)	121.3 (4)	P—C(21)—C(22)	119.6 (3)
C(25)—C(24)—C(27)	120.9 (4)	P—C(31)—C(36)	118.5 (3)
C(32)—C(33)—C(34)	121.8 (5)	C(2)—C(1)—C(6)	109.3 (5)
C(31)—C(36)—C(35)	120.8 (5)	C(2)—C(3)—O	123.5 (5)
C(32)—C(31)—C(36)	118.2 (4)	C(12)—C(13)—C(14)	121.7 (6)
Cl(1)—Tc—Cl(3)	90.4 (1)	C(11)—C(16)—C(15)	120.1 (6)
C(1)—P—C(21)	109.5 (2)	C(12)—C(11)—C(16)	118.5 (4)
C(11)—P—C(31)	107.3 (2)	C(23)—C(24)—C(25)	117.5 (5)
P—C(1)—C(5)	108.4 (5)	C(23)—C(24)—C(27)	121.6 (6)
P—C(11)—C(16)	119.3 (4)	C(31)—C(32)—C(33)	120.2 (6)
P—C(31)—C(32)	122.5 (4)	C(34)—C(35)—C(36)	120.8 (6)
C(2)—C(1)—C(5)	111.4 (5)	C(35)—C(34)—C(37)	120.4 (6)
C(2)—C(3)—C(4)	114.3 (5)		

acetone solution. The compound was recrystallized from DMF. The results of the crystallographic study have shown that the compound is the ionic compound [(*p*-tolyl)$_3$PC(CH$_3$)$_2$CH$_2$COCH$_3$]$_2$[TcCl$_6$]. The surprising cation was produced by the reaction of P(*p*-tolyl)$_3$ with acetone in acid medium. A similar compound was reported with PPh$_3$, which produced under similar conditions [(Ph)$_3$PC(CH$_3$)$_2$CH$_2$CO-CH$_3$][Tc(PPh$_3$)Cl$_5$] (Rochon *et al.*, 1991*a*). The crystal structure of the latter compound has been published by Bandoli *et al.* (1982) who have synthesized the compound by a different method.

The Tc atom of the anion is located on an inversion center. A labelled drawing of the ions is shown in Fig. 2. The bond distances and angles are listed in Table 3. The Tc—Cl bond lengths vary from 2.352 (2) to 2.359 (1) Å and are very similar to those observed in [TcCl$_6$]$^{2-}$ salts of K$^+$ and NH$_4^+$ (Melnik

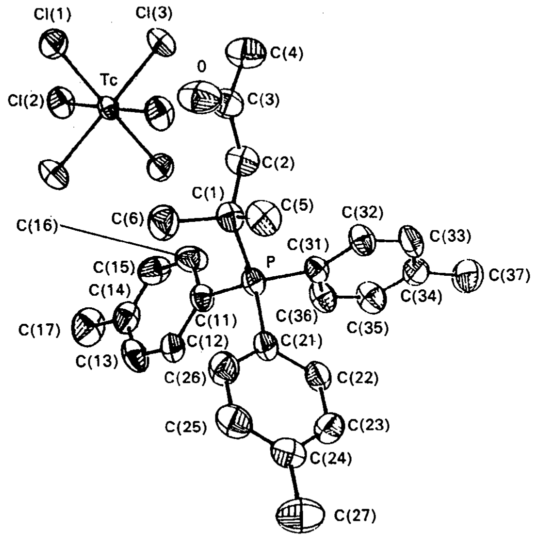

Fig. 2. Labelled diagram of $[(C_7H_7)_3PC(CH_3)_2CH_2COCH_3]_2$-$[TcCl_6]$ (II).

& 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 signficantly longer [1.867 (7) Å], similar to the values observed for $[PPh_3\{C(CH_3)_2CH_2COCH_3\}]$-$[Tc(PPh_3)Cl_5]$ 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) 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.

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Structure of μ_6-Carbido-undecacarbonyldi(μ_3-sulfido)(triphenylphosphine)-*triprismo*-hexacobalt

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Abstract. $[CoC(S)_2(C_{18}H_{15}P)(CO)_{11}]$, 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) Å^3, $Z = 4$, $D_x = 1.854$ 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