

# Bis[1,2-bis(diphenylphosphino)ethane-*P,P'*]- (dithioformato-*S,S'*)technetium tris(benzene) solvate

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## Key indicators

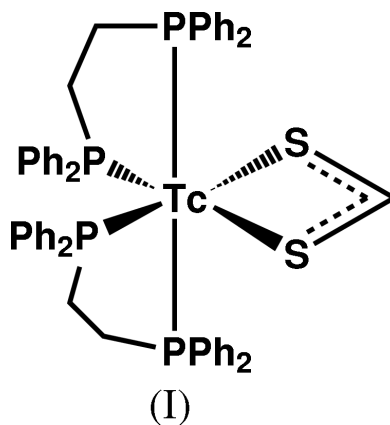
Single-crystal X-ray study  
*T* = 194 K  
 Mean  $\sigma(\text{C}—\text{C})$  = 0.006 Å  
 Disorder in solvent or counterion  
*R* factor = 0.035  
*wR* factor = 0.104  
 Data-to-parameter ratio = 13.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Two Tc-containing products were isolated from the reaction between CS<sub>2</sub> and the electron-deficient complex TcCl(dppe)<sub>2</sub>. The title dithioformate complex, [Tc(S<sub>2</sub>CH)(dppe)<sub>2</sub>]·3C<sub>6</sub>H<sub>6</sub>, where dppe is 1,2-bis(diphenylphosphino)ethane (C<sub>26</sub>H<sub>24</sub>P<sub>2</sub>), exhibits Tc—P bond lengths ranging from 2.3566 (14) to 2.3884 (14) Å, which are little shorter than normally found. The other product is [TcCl(CS)(dppe)<sub>2</sub>], and is the first reported Tc–thiocarbonyl complex.

## Comment

The title compound, (I), was prepared during an examination of the reactivity of the 16-electron complex [TcCl(dppe)<sub>2</sub>], where dppe is 1,2-bis(diphenylphosphino)ethane (Burrell *et al.*, 1994). It is the first structural characterization of the dithioformate ligand on Tc. Only one other Tc–dithioformate complex, [Tc(S<sub>2</sub>CH)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], has been previously reported, but its structure was not determined (Cook *et al.*, 1995).



The structure of the title compound (Fig. 1) is quite similar to isoelectronic, and isostructural [Fe(S<sub>2</sub>CH)(depe)<sub>2</sub>]<sup>+</sup> (Bianchini *et al.*, 1982), and the closely related technetium(II) complexes [Tc(S<sub>2</sub>CNMe<sub>2</sub>)(depe)<sub>2</sub>]<sup>+</sup> (Okamoto *et al.*, 1993) and [Tc(S<sub>2</sub>CNMe<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> (Rochon *et al.*, 1992). The Tc—P bond lengths range from 2.3566 (14) to 2.3884 (14) Å, which are little shorter than normally observed. A search of the Cambridge Structural Database (Allen & Kennard, 1993) indicates that most Tc—P bonds range from 2.39 to 2.50 Å, with a mean value of 2.44 Å.

## Experimental

[TcCl(dppe)<sub>2</sub>] (100 mg) was added to a benzene (50 ml) solution containing CS<sub>2</sub> (0.2 ml) and triphenylphosphine (50 mg). This mixture was heated to reflux for 2 min and then allowed to cool. Hexane was added to the solution and then the mixture was allowed

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to stand. Over time, a mixture of orange and yellow crystals were deposited. The orange crystals proved to be  $[\text{Tc}(\text{S}_2\text{CH})(\text{dppe})_2] \cdot 3\text{C}_6\text{H}_6$  ( $\text{C}_{71}\text{H}_{67}\text{P}_4\text{S}_2\text{Tc}$ ).

#### Crystal data

$[\text{Tc}(\text{CHS}_2)(\text{C}_{26}\text{H}_{24}\text{P}_2)_2] \cdot 3\text{C}_6\text{H}_6$	$Z = 2$
$M_r = 1207.2$	$D_x = 1.35 \text{ Mg m}^{-3}$
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 14.132$ (4) Å	Cell parameters from 25 reflections
$b = 14.738$ (6) Å	$\theta = 7.6\text{--}11.9^\circ$
$c = 17.031$ (4) Å	$\mu = 0.46 \text{ mm}^{-1}$
$\alpha = 65.79$ (3)°	$T = 193 \text{ K}$
$\beta = 88.10$ (3)°	Block, red–orange
$\gamma = 67.88$ (3)°	$0.35 \times 0.23 \times 0.15 \text{ mm}$
$V = 2966$ (2) Å <sup>3</sup>	

#### Data collection

Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.029$
$\omega$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: $\psi$ scan ( <i>SHELXTL-Plus</i> ; Siemens, 1990)	$h = 0 \rightarrow 16$
$T_{\text{min}} = 0.854$ , $T_{\text{max}} = 0.934$	$k = -16 \rightarrow 17$
10 893 measured reflections	$l = -20 \rightarrow 20$
10431 independent reflections	3 standard reflections
7752 reflections with $I > 2\sigma(I)$	frequency: 120 min
	intensity decay: 8%

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.5423P]$
$R(F) = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.008$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
10431 reflections	$\Delta\rho_{\text{min}} = -0.43 \text{ e \AA}^{-3}$
768 parameters	
H atoms treated by a mixture of independent and constrained refinement	

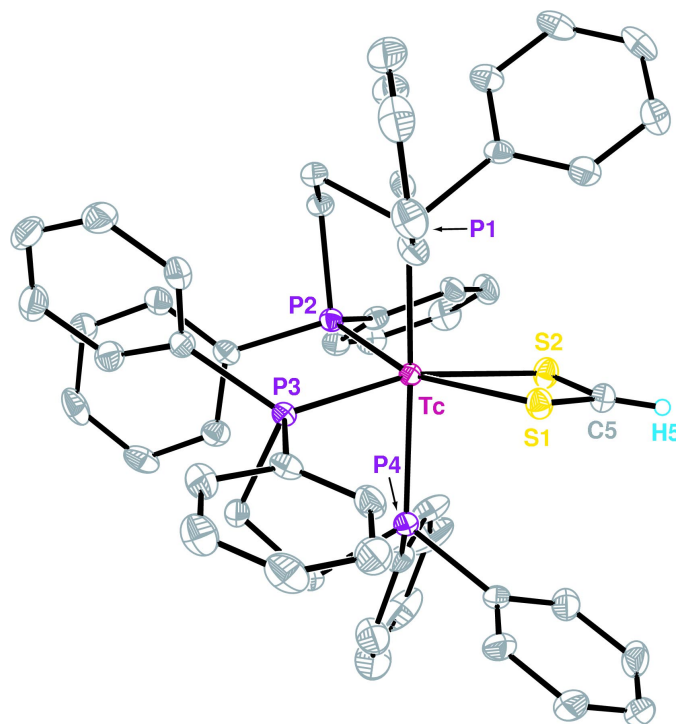
Two of the benzene solvate molecules are disordered and each is modeled over two sites (68:32 and 73:27). The 1,1- and 1,3-distances, as well as the  $U_{ij}$  components of bonded or closely spaced disordered atoms are restrained to be similar. Despite the restraints, three atoms exhibit unusual elongation, and two of these (C118 and C120) are refined isotropically. All other non-H atoms are refined anisotropically. The dithioformate H atom (H5) was located in a difference map, and its coordinates were allowed to refine, with  $U_{\text{iso}}(\text{H})$  equal to  $1.5U_{\text{iso}}(\text{C5})$ . All other H atoms were placed in calculated positions, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they were attached.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1993);

**Table 1**

Selected geometric parameters (Å, °).

Tc–S1	2.4866 (14)	Tc–P2	2.3632 (14)
Tc–S2	2.4548 (15)	Tc–P3	2.3566 (14)
Tc–P1	2.3650 (14)	Tc–P4	2.3884 (14)
S1–Tc–S2	68.38 (4)	S2–Tc–P4	85.93 (5)
S1–Tc–P1	89.52 (4)	P1–Tc–P2	82.05 (4)
S1–Tc–P2	160.79 (5)	P1–Tc–P3	94.05 (4)
S1–Tc–P3	103.41 (5)	P1–Tc–P4	175.03 (5)
S1–Tc–P4	89.41 (4)	P2–Tc–P3	94.42 (5)
S2–Tc–P1	98.18 (5)	P2–Tc–P4	100.39 (4)
S2–Tc–P2	95.66 (5)	P3–Tc–P4	81.48 (4)
S2–Tc–P3	165.10 (5)	S1–C5–S2	112.5 (3)



**Figure 1**

The molecular structure of the title compound showing 50% probability displacement ellipsoids. The benzene solvate molecules, and all H atoms, except H5 have been omitted for clarity.

program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *PLATON* (Spek, 2000).

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