

$[\text{TcCl}(\text{CS})(\text{dppe})_2] \cdot \text{C}_6\text{H}_6$ Jeffrey C. Bryan,^{a*} Anthony K. Burrell^b and Gregory J. Kubas^c

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Key indicators

Single-crystal X-ray study

 $T = 203 \text{ K}$ Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

Disorder in main residue

 R factor = 0.032 wR factor = 0.098

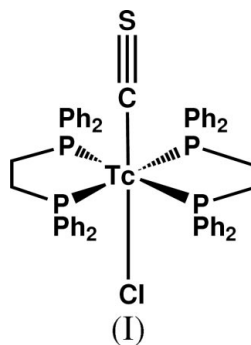
Data-to-parameter ratio = 19.4

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

The title compound, chlorobis[1,2-ethanediylbis(diphenylphosphine)-*P,P'*](thiocarbonyl-*C*)technetium benzene solvate, $[\text{TcCl}(\text{C}_{46}\text{H}_{42}\text{P}_4)(\text{CS})] \cdot \text{C}_6\text{H}_6$, was obtained as one of two Tc-containing products isolated from the reaction between CS_2 and the electron-deficient complex $[\text{TcCl}(\text{th})>(\text{dppe})_2]$, where dppe is 1,2-ethanediylbis(diphenylphosphine). The structure exhibits an unusually short Tc—C distance [1.819 (6) Å], suggesting some multiple-bond character.

Comment

Two new compounds were prepared during an examination of the reactivity of the 16-electron complex $[\text{TcCl}(\text{dppe})_2]$, where dppe is 1,2-ethanediylbis(diphenylphosphine) (Burrell, Kubas & Bryan, 1994). Both a dithioformate complex, $[\text{Tc}(\text{th})>(\text{S}_2\text{CH})(\text{dppe})_2]$ (Bryan *et al.*, 2001) and a thiocarbonyl complex $[\text{TcCl}(\text{CS})(\text{dppe})_2]$ were formed. The latter, (I), is the topic of this paper and is the first reported example of a Tc—thiocarbonyl complex.



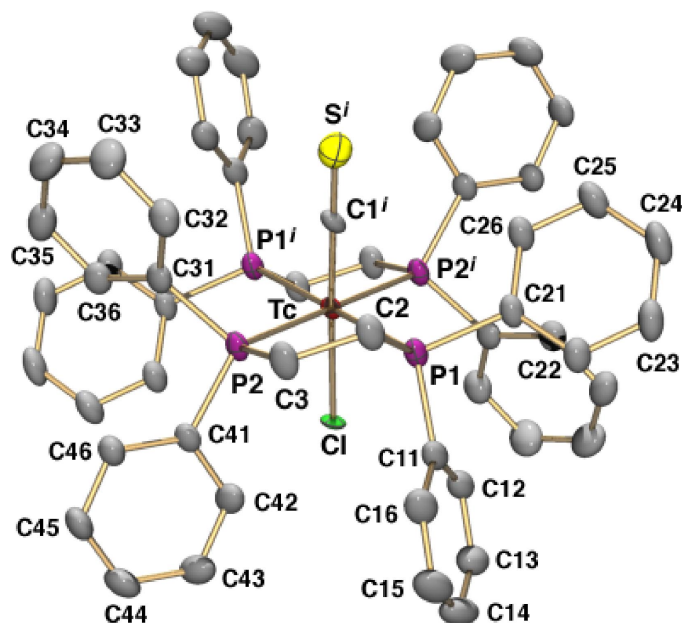
The structure can be solved in $P1$ with $Z = 1$, but a high degree of correlation is observed, and the Cl and CS ligands are disordered (50:50) superimposed on each other. There is an apparent inversion centre at Tc, strongly suggesting that the correct space group is $P\bar{1}$. When solved in $P\bar{1}$, only half of the molecule makes up the asymmetric unit, with the metal ion located at the crystallographic inversion centre. The chloride and thiocarbonyl ligands are modeled with equal occupancy factors (50:50) at the same site of ligation on Tc, but are assumed to be different on either side of the inversion centre, as illustrated in Fig. 1. The Tc—C bond length is apparently quite short at 1.819 (6) Å, and may indicate some level of multiple bonding, although this bond distance may be affected by the disorder. The only published example of a Tc=C is the closely related $[\text{TcCl}(\text{CCHPh})\text{Cl}(\text{dppe})_2]$ (Burrell, Bryan & Kubas, 1994), which is 1.861 (9) Å. For comparison, Tc—CO

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Dedicated to Warren R. Roper.


Figure 1

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

bond lengths typically range from 1.88 to 2.00 Å, with a mean value of 1.93 Å (Allen & Kennard, 1993). Otherwise, the title complex is structurally quite similar to the isoelectronic [ReCl(CO)(dppe)₂] (da Silva *et al.*, 1998).

Experimental

[TcCl(dppe)₂] (100 mg) was added to a benzene (50 ml) solution containing CS₂ (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 to stand. Over time, a mixture of orange and yellow crystals were deposited. The yellow crystals proved to be [TcCl(CS)(dppe)₂] \cdot C₆H₆.

Crystal data

[TcCl(C₄₆H₄₂P₄)(CS)] \cdot C₆H₆
 $M_r = 1053.3$
 Triclinic, $P\bar{1}$
 $a = 10.3872$ (10) Å
 $b = 10.5518$ (9) Å
 $c = 12.8953$ (11) Å
 $\alpha = 67.185$ (6)°
 $\beta = 72.620$ (9)°
 $\gamma = 83.849$ (8)°
 $V = 1243.3$ (2) Å³

$Z = 1$
 $D_x = 1.41$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 6.7$ – 26.0 °
 $\mu = 0.55$ mm⁻¹
 $T = 203$ K
 Plate, yellow
 $0.58 \times 0.51 \times 0.15$ mm

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (SHELXTL-Plus; Siemens, 1990)
 $T_{\min} = 0.732$, $T_{\max} = 0.897$
 7126 measured reflections
 6069 independent reflections
 5372 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 29.0$ °
 $h = -1 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -17 \rightarrow 17$
 3 standard reflections
 every 97 reflections
 intensity decay: 1.24%

Refinement

Refinement on F^2
 $R(F) = 0.032$
 $wR(F^2) = 0.098$
 $S = 1.24$
 6069 reflections
 313 parameters
 H-atom parameters not refined

$$w = 1/[\sigma^2(F_o^2) + (0.0560P)^2 + 0.0349P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.92 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Tc—Cl	2.538 (2)	Tc—Cl	1.819 (6)
Tc—P1	2.4091 (6)	S—Cl	1.468 (7)
Tc—P2	2.4355 (6)		
Cl—Tc—P1	95.43 (3)	P1—Tc—Cl	96.3 (2)
Cl—Tc—P2	98.00 (3)	P2—Tc—Cl	96.3 (2)
Cl—Tc—Cl ⁱ	178.0 (2)	Tc—Cl—S	178.1 (3)
P1—Tc—P2	80.67 (2)	P1—Cl1—C16	123.7 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

All H atoms were placed in calculated positions, refined using a riding model, and given an isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they were attached.

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 2000).

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