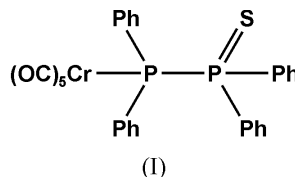


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Key indicators

Single-crystal X-ray study
T = 178 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.040
wR factor = 0.108
Data-to-parameter ratio = 13.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Pentacarbonyl(tetraphenyldiphosphine
monosulfide-*P*)chromium(0)In the title compound, $[\text{Cr}(\text{C}_{24}\text{H}_{20}\text{P}_2\text{S})(\text{CO})_5]$, the key bond lengths are P1–P2 2.2659 (15), P2–S 1.9531 (15), P1–C 1.830, 1.833 (3), P2–C 1.821, 1.822 (3) and P1–Cr 2.3921 (13) Å. The conformation about the P–P bond is defined by the torsion angle S–P2–P1–Cr of $-58.60 (7)^\circ$.

Comment

The title compound, (I), arose during studies (see *Experimental*) of thioureas substituted with phosphorus-containing groups (Farkens, 1991). It was characterized by this structure determination.

The molecular structure of (I) is shown in Fig. 1. A search of the Cambridge Structural Database (CSD, Version of April 2002; Allen & Kennard, 1993) revealed no other complexes of any tetra(organyl)diphosphine monosulfide (in the strict sense of a compound containing a P–P bond). The key bond lengths are P1–P2 2.2659 (15), P2–S 1.9531 (15), P1–C 1.830, 1.833 (3) and P2–C 1.821 1.822 (3) Å. These may be compared, although the two systems clearly differ chemically in many respects, with values for uncomplexed tetramethyldiphosphane monosulfide (Gruber *et al.*, 1990): P–P 2.201 (1), P–S 1.970 (1), P^{III}–C 1.830 and 1.834 (1), and P(S)–C 1.803 and 1.803 (1) Å. The P–P bond in (I) may be regarded as long, and it is reasonable to propose steric effects as the cause. A CSD search revealed 57 structures with (C)₂P–P(C)₂ single bonds, involving 69 bonds in the range 2.104–2.310 Å (average 2.216 Å).

The P–Cr distance is 2.3921 (13) Å, and the Cr–C bond *trans* to Cr–P is by far the shortest, at 1.865 (4) Å, *cf.* average 1.903 Å for the other four Cr–C bonds. The conformation about the P–P bond is defined by the torsion angle S–P2–P1–Cr of $-58.60 (7)^\circ$ (in the above-mentioned diphosphine monosulfide, the S atom is *trans* to the lone pair at the other phosphorus). As expected, the largest angles at phosphorus are those involving the Cr atom at P1 and the S atom at P2.

Two short H···O contacts could reasonably be interpreted as weak hydrogen bonds (Table 2).

Experimental

The reaction between (norbornadiene)Cr(CO)₄ and *N,N'*-bis(diphenylphosphino)-*N,N'*-dimethylthiourea in dichloromethane led to

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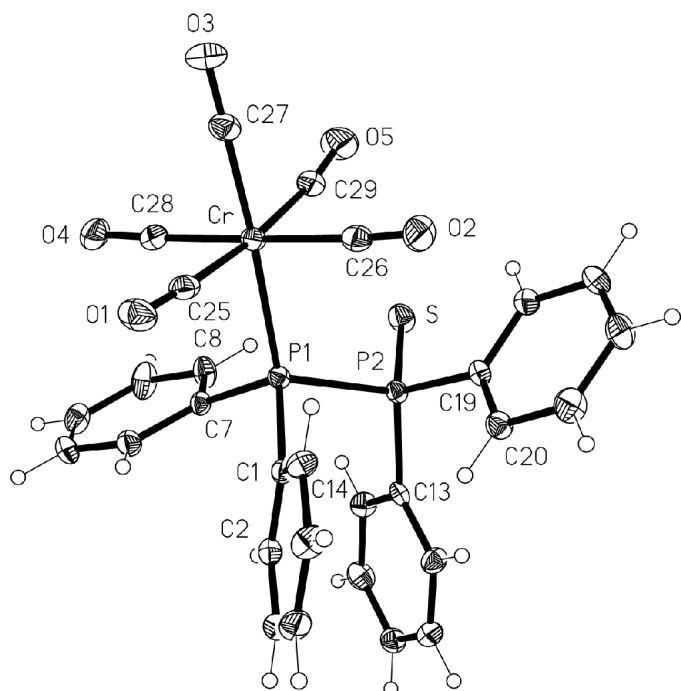


Figure 1
The molecule of compound (I) in the crystal. Displacement ellipsoids represent 30% probability levels. H-atom radii are arbitrary.

a complex mixture of products. The mixture was dissolved in diethyl ether, from which the title compound crystallized in 13% yield (Farkens, 1991). The decomposition of the thiourea to tetraphenyl-diphosphine monosulfide has been observed before in our laboratory (Gruber, 1989).

Crystal data

$[\text{Cr}(\text{C}_{24}\text{H}_{20}\text{P}_2\text{S})(\text{CO})_2]$	$Z = 2$
$M_r = 594.45$	$D_x = 1.466 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.840 (3) \text{ \AA}$	Cell parameters from 50 reflections
$b = 10.089 (5) \text{ \AA}$	$\theta = 10\text{--}11.5^\circ$
$c = 14.967 (6) \text{ \AA}$	$\mu = 0.66 \text{ mm}^{-1}$
$\alpha = 77.90 (3)^\circ$	$T = 178 (2) \text{ K}$
$\beta = 84.43 (3)^\circ$	Tablet, yellow
$\gamma = 68.02 (3)^\circ$	$0.5 \times 0.5 \times 0.2 \text{ mm}$
$V = 1347.0 (10) \text{ \AA}^3$	

Data collection

Nicolet R3 diffractometer	$R_{\text{int}} = 0.038$
ω scans	$\theta_{\text{max}} = 25.1^\circ$
Absorption correction: ψ scan (<i>XEMP</i> ; Nicolet, 1987)	$h = -11 \rightarrow 11$
$T_{\text{min}} = 0.801$, $T_{\text{max}} = 0.991$	$k = -11 \rightarrow 11$
5120 measured reflections	$l = -12 \rightarrow 17$
4578 independent reflections	3 standard reflections
3476 reflections with $I > 2\sigma(I)$	every 147 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 1.6663P]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
4578 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
343 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cr—C27	1.865 (4)	S—P2	1.9531 (15)
Cr—C25	1.893 (4)	P1—C1	1.830 (3)
Cr—C28	1.895 (4)	P1—C7	1.833 (3)
Cr—C26	1.909 (4)	P1—P2	2.2659 (15)
Cr—C29	1.916 (4)	P2—C13	1.821 (3)
Cr—P1	2.3921 (13)	P2—C19	1.822 (3)
C27—Cr—C25	88.48 (15)	C29—Cr—P1	95.75 (11)
C27—Cr—C28	88.55 (15)	C1—P1—C7	103.54 (14)
C25—Cr—C28	87.44 (15)	C1—P1—P2	101.21 (10)
C27—Cr—C26	89.65 (15)	C7—P1—P2	104.56 (10)
C25—Cr—C26	91.50 (15)	C1—P1—Cr	119.02 (11)
C28—Cr—C26	177.94 (14)	C7—P1—Cr	110.78 (10)
C27—Cr—C29	85.89 (15)	P2—P1—Cr	116.02 (5)
C25—Cr—C29	173.94 (14)	C13—P2—C19	110.90 (14)
C28—Cr—C29	90.19 (15)	C13—P2—S	111.01 (11)
C26—Cr—C29	90.69 (16)	C19—P2—S	111.67 (11)
C27—Cr—P1	176.55 (11)	C13—P2—P1	107.35 (10)
C25—Cr—P1	89.77 (10)	C19—P2—P1	103.03 (11)
C28—Cr—P1	88.40 (10)	S—P2—P1	112.55 (6)
C26—Cr—P1	93.36 (10)		
C1—P1—P2—C13	48.63 (15)	Cr—P1—P2—C19	61.83 (11)
C7—P1—P2—C13	−58.72 (15)	C1—P1—P2—S	171.07 (11)
Cr—P1—P2—C13	178.96 (10)	C7—P1—P2—S	63.72 (11)
C1—P1—P2—C19	−68.50 (15)	Cr—P1—P2—S	−58.60 (7)
C7—P1—P2—C19	−175.85 (14)		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C22—H22 \cdots O2 ⁱ	0.95	2.65	3.581 (4)	166
C21—H21 \cdots O4 ⁱⁱ	0.95	2.57	3.426 (5)	149

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 + x, y, z$.

H atoms were included using a riding model with fixed C—H bond lengths of 0.95 \AA ; $U_{\text{iso}}(\text{H})$ values were fixed at 1.2 times the U_{eq} of the parent atom.

Data collection: *P3* (Nicolet, 1987); cell refinement: *P3*; data reduction: *XDISK* (Nicolet, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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