

Tetracarbonyl(diphenyldithio- phosphinato-*S,S'*)rhenium(I)

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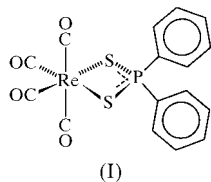
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The title compound consists of $[\text{Re}(\text{C}_{12}\text{H}_{10}\text{PS}_2)(\text{CO})_4]$ molecules in which the Re atom is octahedrally coordinated by four carbonyl groups and two dithiophosphinate S atoms. The main coordination distortion is imposed by the ligand bite angle of $78.29(4)^\circ$. The bidentate coordination of the dithiophosphinate ligand involves almost equal Re—S [2.5366 (15) and 2.5535 (14) Å] and P—S distances [2.0100 (19) and 2.0212 (19) Å].

Comment

The dithiophosphinate ligand is a very versatile chelating ligand in transition metal coordination chemistry. Consequently, a great number of metal and organometallic complexes are known (Haiduc *et al.*, 1995). However, the corresponding derivatives of carbonyl complexes of group seven are rather scarce. This is surprising because they have been used as suitable precursors in the synthesis of dinuclear (Thiele *et al.*, 1974*a*, and references therein) or *cis*-disubstituted complexes (Lindner & Berke, 1972). Additionally, structural knowledge of the carbonyl complexes of group seven metals can be applied in comparative studies of other dithioligand complexes with interesting properties, such as luminescence (Leirer *et al.*, 1998). As part of a study of the coordination behaviour of the $[\text{Re}(\text{CO})_3]^+$ and $[\text{Re}(\text{CO})_4]^+$ moieties, we have synthesized $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CO})_4]$, (I), by a similar method to that of Lindner & Matejcek (1970).



The structure of (I) consists of isolated $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CO})_4]$ molecules with no unusually short contacts. The dithiophosphinate ligand links to rhenium in an almost symmetrical

bidentate mode. The Re—S distances are close to those found in the dimeric $[\text{Re}_2(\mu\text{-S}_2\text{PET}_2)_2(\text{CO})_6]$ complex [2.535 (8)–2.570 (11) Å; Thiele *et al.*, 1974*a*], but slightly longer than in the dithiocarbamate analogues $[\text{Re}\{\text{S}_2\text{CN}(\text{H})\text{Ph}\}(\text{CO})_3(\text{PPh}_3)_2]$ [2.512 (5) and 2.525 Å; Rossi *et al.*, 1987] and $[\text{Re}\{\text{S}_2\text{CN}(\text{H})\text{Tiaz}\}(\text{CO})_2(\text{PPh}_3)]$ (Tiaz is thiazol-2-yl; Rossi *et al.*, 1988), the dithiocarboxylate $[\text{Re}(\text{S}_2\text{CPh})(\text{CO})_4]$ (2.49 Å; Thiele & Liehr, 1971) or the trithiocarbonate $[\text{Re}_4(\text{CS}_3)_2(\text{CO})_{16}]$ (2.487–2.514 Å; Thiele *et al.*, 1974*b*). The Re—C distances corresponding to carbonyl groups *trans* to the S atoms are systematically shorter. In agreement with the latter, the corresponding C—O distances are slightly increased. Similar effects have been observed in $[\text{Mn}(\text{S}_2\text{PET}_2)(\text{CO})_4]$ (Almond *et al.*, 1995) and suggest some π -donor character of the dithiophosphinate ligand.

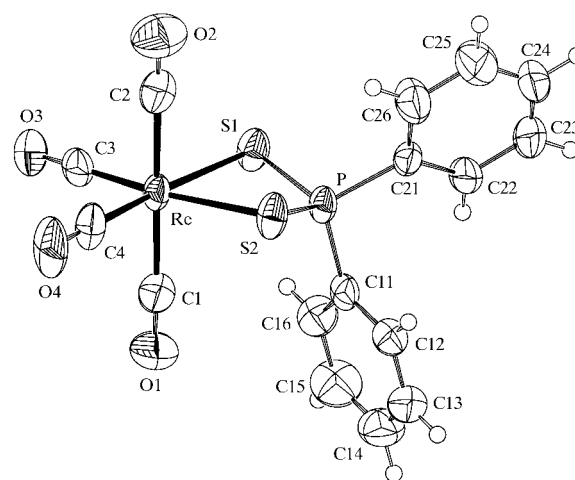


Figure 1
ZORTEP (Zsolnai & Huttner, 1994) drawing of $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CO})_4]$. Atoms represented as displacement ellipsoids are drawn at the 30% probability level.

The P atom lies 0.532 (2) Å out of the plane defined by the Re and S atoms and the two carbonyl groups *trans* to the dithiophosphinate ligand (Re/C3/O3/C4/O4/S1/S2, r.m.s. deviation = 0.017 Å). The chelation mode places a phenyl group almost parallel to the vector Re—C1—O1 (Fig. 1), whereby the shortest distances C1...C16 and C1...C11 [3.417 (10) and 3.497 (9) Å, respectively] are slightly longer than double the van der Waals radius (1.70 Å) of carbon (Spek, 2000). The resulting four-membered ReS_2P ring is not planar; the angles are S1—Re—S2 $78.29(4)^\circ$, P—S1—Re $85.52(6)^\circ$, P—S2—Re $84.85(6)^\circ$ and S1—P—S2 $105.71(8)^\circ$, and the fold angle about the S1...S2 vector is $26.47(6)^\circ$.

The coordination polyhedron around the Re atom can be described as a slightly distorted octahedron, the main distortion being imposed by the ligand bite [S1—Re—S2 $78.29(4)^\circ$]. The P—S distances are practically identical and consistent with the bidentate character of the ligand. They are also close to those found in $[\text{Mn}(\text{S}_2\text{PET}_2)(\text{CO})_4]$ [2.004 (4) and 2.008 (4) Å; Almond *et al.*, 1995].

Experimental

The title compound was obtained by a similar method to that reported by Lindner & Matejcek (1970) using $[\text{ReBr}(\text{CO})_5]$ and HS_2PPh_2 in toluene. Single crystals of the compound were obtained by storing the mother liquor at 269 K for a few days. Analysis found: C 33.1, H 1.9, S 10.4%. $\text{C}_{16}\text{H}_{10}\text{O}_4\text{PReS}_2$ requires: C 33.2, H 1.7, S 11.0%. Mass spectrum (FAB-NBA; m/z , %): $|M|^+$ 453 (31), $|M - \text{CO}|^+$ 424 (100), $|M - 2\text{CO}|^+$ 396 (19), $|M - 3\text{CO}|^+$ 368 (17), $|M - 4\text{CO}|^+$ 340 (11). IR (Raman) spectrum (KBr, cm^{-1}): 1925 (s) [1927 (s)], 1983 (m) [1976 (s)], 2004 (m) [1991 (m)], 2102 (s) [2100 (s)] $\nu(\text{CO})$, 571 (s) [none] $\nu_{\text{asym}}(\text{PS}_2)$, 493 (s) [495 (s)] $\nu_{\text{sym}}(\text{PS}_2)$. ^{13}C NMR spectrum (CDCl_3 , p.p.m.): 184.4, 184.2 $\delta(\text{CO})$. $\delta(^{31}\text{P}) = 124.3$ p.p.m.

Crystal data

$[\text{Re}(\text{C}_{12}\text{H}_{10}\text{PS}_2)(\text{CO})_4]$	Mo $K\alpha$ radiation
$M_r = 547.53$	Cell parameters from 23 344 reflections
Orthorhombic, $Pbca$	
$a = 16.11600$ (10) Å	$\theta = 2.3\text{--}28.3$
$b = 12.8286$ (2) Å	$\mu = 7.015$ mm^{-1}
$c = 17.5930$ (3) Å	$T = 293$ (2) K
$V = 3637.28$ (9) Å ³	Prism, light brown
$Z = 8$	$0.20 \times 0.15 \times 0.10$ mm
$D_x = 2.000$ Mg m^{-3}	

Data collection

CCD area-detector diffractometer	3181 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.085$
Absorption correction: empirical	$\theta_{\text{max}} = 28.30^\circ$
(<i>SADABS</i> ; Sheldrick, 1996)	$h = -21 \rightarrow 21$
$T_{\text{min}} = 0.271$, $T_{\text{max}} = 0.551$	$k = -13 \rightarrow 17$
23 344 measured reflections	$l = -23 \rightarrow 21$
4518 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2]$
$wR(F^2) = 0.098$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.977$	$(\Delta/\sigma)_{\text{max}} = 0.002$
4518 reflections	$\Delta\rho_{\text{max}} = 1.4$ e Å ⁻³
217 parameters	$\Delta\rho_{\text{min}} = -3.52$ e Å ⁻³

H atoms were geometrically calculated and refined using a riding model ($\text{C}-\text{H} = 0.93$ Å). The maximum and minimum difference peaks lie 0.94 and 0.87 Å, respectively, from the Re atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

Table 1

Selected geometric parameters (Å, °).

Re—C3	1.920 (6)	S1—P	2.0100 (19)
Re—C4	1.929 (7)	S2—P	2.0212 (19)
Re—C1	1.993 (7)	O1—C1	1.128 (7)
Re—C2	2.004 (7)	O2—C2	1.123 (8)
Re—S1	2.5366 (15)	O3—C3	1.148 (7)
Re—S2	2.5535 (14)	O4—C4	1.130 (7)
C3—Re—C4	91.1 (2)	C1—Re—S1	93.6 (2)
C3—Re—C1	90.7 (2)	C2—Re—S1	87.2 (2)
C4—Re—C1	86.6 (3)	C3—Re—S2	172.41 (17)
C3—Re—C2	91.3 (2)	C4—Re—S2	96.28 (18)
C4—Re—C2	92.4 (3)	C1—Re—S2	91.43 (19)
C1—Re—C2	177.8 (3)	C2—Re—S2	86.80 (17)
C3—Re—S1	94.30 (17)	S1—Re—S2	78.29 (4)
C4—Re—S1	174.57 (18)	S1—P—S2	105.71 (8)

SHELXTL; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1448). Services for accessing these data are described at the back of the journal.

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