Some red-brown needles were isolated and mounted in evacuated glass capilliaries. After checking for crystal quality with the Weissenberg technique, a crystal suitable for further analysis was selected for data collection at 295 (1) K. Unit-cell parameters were determined from an automatic search routine. Both Lorentz and polarization corrections were applied, as well as correction based on decay in the standard reflections.

The non-centrosymmetric space group *C*2 was the initial choice based upon reflection statistics (*SHELXS*86; Sheldrick, 1985). Nearly all reflections were observed and a crystallographic mirror plane was detected during refinement. The centrosymmetric space group *C*2/*m* is, therefore, the correct space group. The structure consists of mononuclear tantalum complexes surrounded by four Cl atoms [Ta—Cl = 2.370 (2) Å] in an almost square-planar arrangement with two pyridine ligands [Ta—N = 2.222 (7) Å], which reside on the crystallographic mirror plane, completing the coordination octahedron in a *trans* configuration. All H atoms were of the riding-model type with a distance of 0.96 Å and fixed isotropic displacement parameters set equal to that of the adjacent C atoms.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, atomic parameters used in the extended Hückel calculations and crystallographic data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71257 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1043]

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Structure of *trans*-Carbonyl(thiocyanato-*N*)-bis(triethylphosphine)rhodium(I)

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Abstract

The title compound is a four-coordinate Rh^{I} complex in which the metal is ligated by two mutually *trans* triethylphosphines, a carbonyl and an isothiocyanate group. The molecule lies on a crystallographic twofold axis which passes through the metal, the carbonyl and the isothiocyanate group. Steric factors play a part in determining the coordination mode of the NCS$^-$ ligand: in particular, the bulk of the triethylphosphine ligands disfavours linkage through the larger S atom, whose preference for non-linear coordination would also cause steric problems.

Comment

On the basis of the 'soft' nature of both sulfur and rhodium(I) (Purcell & Kotz, 1977), one would expect that the thiocyanate ligand would be S bonded to the metal centre. However, it has been shown that the mode of binding is very sensitive to steric factors and can indeed be controlled, for example by adjusting the bite angle of a diphosphine chelating a palladium(II) centre (Beran, Mathew, Palenik & Steffen, 1975). Interpretation of the IR spectrum of the title compound (Jennings & Wojcicki, 1967) suggested linkage through the N atom of the NCS$^-$ group (Norbury & Sinha, 1970), a result which we have confirmed. The Rh—CO bond length of 1.775 (6) Å is rather shorter than in most of the related *trans*-[Rh(CO)X(PR_3)$_2$] (X = Cl, I) complexes (Basson, Leipoldt & Roodt, 1990; Blum, Eisen, Jurgis & Schumann, 1990; Ceriotti, Ciani & Sironi, 1983; Dahan & Choukroun, 1985; Rheingold & Geib, 1987; Monge, Gutierrez-Puebla, Heras & Pinilla, 1983; Heisler, Pickardt & Schumann, 1977). Although the structure of *trans*-[Rh(CO)Cl(PEt$_3$)$_2$] has not been reported, these complexes contain phosphines with a range of cone angles (122–182°) which bracket that of PEt$_3$ (132°) (Tolman, 1977). The

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correlation of Rh—CO bond length with cone angle predicts an Rh—CO bond of *ca* 1.80 Å in *trans*-[Rh(CO)Cl(PEt$_3$)$_2$]. The shortness of this bond in the title compound may result from electronic differences between halide and isothiocyanate.

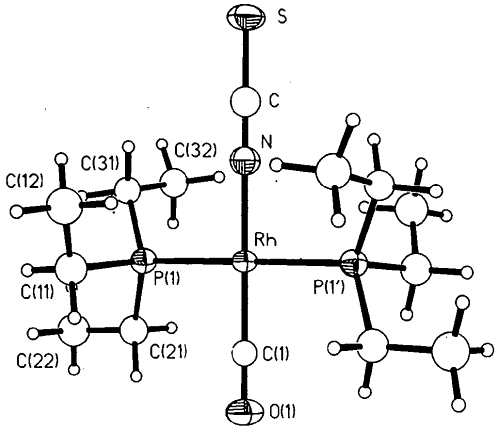

Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 30% probability level. The molecule lies on a crystallographic twofold axis which passes through S, C, N, Rh, C(1) and O(1) and relates the two phosphine ligands coordinated through P(1) and P(1′).

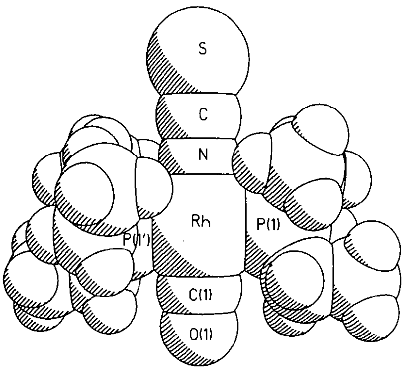

Fig. 2. A space-filling plot of the molecule showing the close steric fit of the ligands around the metal centre.

Experimental

Crystal data

[Rh(NCS)(C$_6$H$_{15}$P)$_2$(CO)]
M_r = 425.3
Monoclinic
$C2/c$
a = 13.4022 (20) Å
b = 12.0313 (17) Å
c = 13.9832 (24) Å
β = 117.899 (10)°
V = 1992.7 Å^3
Z = 4
D_x = 1.417 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54184 Å

Cell parameters from 31 reflections
θ = 17.5–20.0°
μ = 9.576 mm^{-1}
T = 298 K
Column
0.4 × 0.2 × 0.2 mm
Yellow
Crystal source: metathesis of [RhCl(PEt$_3$)$_2$(CO)] with KNCS in acetone; crystals from hot petroleum ether

Data collection

Stoe Stadi-4 four-circle diffractometer
ω-2θ scans
Absorption correction: empirical
T_{min} = 0.1708, T_{max} = 0.2938
1725 measured reflections
1297 independent reflections
1149 observed reflections
[$F \geq 6\sigma(F)$]

R_{int} = 0.014
θ_{max} = 60°
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity variation: no significant variation

Refinement

Refinement on F
Final R = 0.0527
wR = 0.0750
S = 1.247
1149 reflections
59 parameters
H-atom parameters not refined
$w = [\sigma^2(F) + 0.000315F^2]^{-1}$
$(\Delta/\sigma)_{max}$ = 0.005

$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}
Extinction correction: secondary, isotropic
Extinction coefficient: 1.7 (5) × 10^{-7}
Atomic scattering factors from Cromer & Mann (1968) for Rh, others inlaid in *SHELX76*

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Rh	0.0	0.23973 (6)	0.25	0.0392 (7)
N	0.0	0.4049 (8)	0.25	0.077 (9)
S	0.0	0.6407 (3)	0.25	0.101 (4)
O(1)	0.0	−0.0040 (7)	0.25	0.085 (8)
P(1)	0.04110 (17)	0.23826 (16)	0.10559 (17)	0.0489 (14)
C	0.0	0.5032 (12)	0.25	0.063 (3)
C(1)	0.0	0.0922 (9)	0.25	0.043 (3)
C(11)	−0.0846 (8)	0.2272 (7)	−0.0243 (7)	0.068 (3)
C(12)	−0.1642 (9)	0.3271 (8)	−0.0455 (8)	0.082 (3)
C(21)	0.1267 (8)	0.1173 (7)	0.1064 (7)	0.063 (3)
C(22)	0.1571 (9)	0.1139 (8)	0.0144 (8)	0.080 (3)
C(31)	0.1171 (7)	0.3596 (7)	0.0939 (7)	0.055 (2)
C(32)	0.2344 (7)	0.3764 (8)	0.1916 (7)	0.069 (3)

Table 2. *Geometric parameters* (Å, °)

Rh—N	1.987 (6)	P(1)—C(11)	1.814 (10)
Rh—C(1)	1.775 (6)	P(1)—C(21)	1.849 (10)
Rh—P(1)	2.329 (2)	P(1)—C(31)	1.830 (9)
N—C	1.183 (10)	C(11)—C(12)	1.541 (15)
C—S	1.655 (8)	C(21)—C(22)	1.521 (15)
C(1)—O(1)	1.157 (8)	C(31)—C(32)	1.539 (13)
N—Rh—P(1)	90.43 (18)	C(11)—P(1)—C(21)	103.4 (5)
C(1)—Rh—P(1)	89.6 (2)	C(11)—P(1)—C(31)	105.3 (4)
P(1)—Rh—P(1′)*	179.12 (8)	C(21)—P(1)—C(31)	105.0 (4)
Rh—P(1)—C(11)	112.5 (3)	P(1)—C(11)—C(12)	111.8 (7)
Rh—P(1)—C(21)	113.5 (3)	P(1)—C(21)—C(22)	115.3 (7)
Rh—P(1)—C(31)	116.0 (3)	P(1)—C(31)—C(32)	113.9 (6)

* P(1′) is related to P(1) by the operation of the crystallographic twofold axis at (0, y, 0.25).

Data were collected using an ω-scan width of (1.50 + 0.347tanθ)° and the unit-cell dimensions were refined against 2θ values obtained at $\pm\omega$. The structure was refined by full-matrix least squares and Rh, S, P, O and N atoms were allowed anisotropic thermal motion. The figures were produced using *XP* (*SHELXTL/PC*; Sheldrick, 1990) and molecular geometry calculations utilized *CALC* (Gould & Taylor, 1985). Program used to solve and refine structure: *SHELX*76 (Sheldrick, 1976).

We thank the SERC for support.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71184 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1042]

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8-(*N*,*N*-Di-*p*-toluenesulfonylamino)quinoline

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Abstract

The S atoms exist in distorted tetrahedral geometries with an average S—N bond distance of 1.672 (5) Å. The coordination about the amido N atom is trigonal planar indicating delocalization of π-electron density around this centre.

Comment

The near trigonal planar geometry about the N(8) atom [this atom lies 0.120 (6) Å out of the plane defined by atoms S(1), S(2) and C(8)] is shown in the three trigonal angles of 117.5 (7), 118.6 (7) and 122.2 (5)°. The equivalence of the S—N bond distances [average 1.672 (5) Å], coupled with the planar N(8) centre, suggest delocalization of π-electron density over this chromophore. The elongation of the S(2)—O(3) bond distance to 1.431 (7) Å may indicate the participation of this bond in conjugation; the S(1)—N(8)—S(2)—O(3) torsion angle is 179.4 (6)°. The remaining S—N—S—O torsion angles [50.8 (7), 144.1 (6) and 15.2 (7)°] suggest little participation in conjugation of the other S═O groups [range of S═O distances 1.408 (8)-1.415 (7) Å]. The S(1)—N(8)—C(8)—C(7) torsion angle of −82 (1)° also indicates that the quinoline residue is not involved in conjugation to the O═S—N—S moiety.

The structure is molecular with the closest intermolecular contact (2.381 Å) occurring between H(17) and H(17′) (symmetry operation: $-x$, $1-y$, $-z$). There are some weaker contacts involving the O atoms, *i.e.* O(3)···H(4″) 2.389 Å (symmetry operation: $0.5-x$, $1-y$, $0.5+z$) and O(1)···H(11‴) 2.482 Å (symmetry operation: x, $0.5-y$, $-0.5+z$); it is therefore unlikely that the presence of intermolecular contacts accounts for the elongation of the S(2)═O(3) bond distance relative to the remaining S═O distances.

Geometric parameters of the the title compound and of the parent compound, *i.e.* 8-toluenesulfonamido-

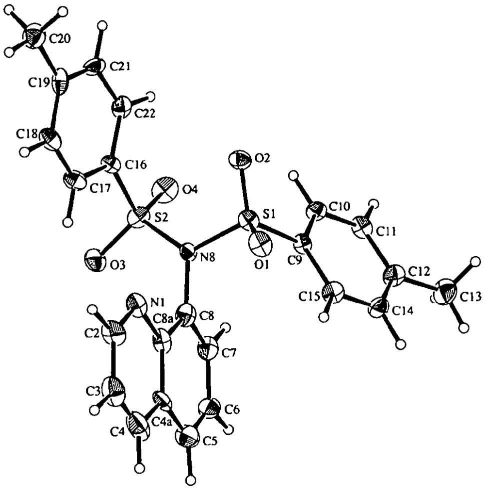

Fig. 1. Molecular structure of the title compound showing the crystallographic numbering scheme; diagram drawn at 20% probability levels (Johnson, 1976).