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Octacarbonyl-μ-dicyclohexylphosphido-μ-*N*,*N*-diethyldithiocarbamato-dirhenium

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Key indicators

Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.018 Å
R factor = 0.051
wR factor = 0.149
Data-to-parameter ratio = 19.7

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

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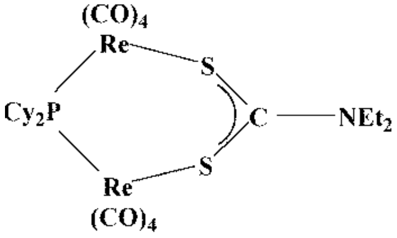
The title compound, $[Re_2\{\mu\text{-}S_2NC(Et_2)\}(\mu\text{-}PCy_2)(CO)_8]$ or $[Re_2(C_5H_{10}NS_2)(C_{12}H_{22}P)(CO)_8]$, is the first structurally characterized rhenium complex with a bridging dithiocarbamate ligand. The Re$\cdots$Re distance is non-bonding.

Comment

The bromo bridge in $Re_2(\mu\text{-}Br)(\mu\text{-}PCy_2)(CO)_8$ is easily substituted by thiolate ligands giving phosphido-thiolato-bridged dirhenium complexes of the general formula $Re_2(\mu\text{-}PCy_2)(\mu\text{-}SR)(CO)_8$ (Egold *et al.*, 2001). We expected the former complex to react in a completely analogous manner with sodium diethyldithiocarbamate. However, this reaction gave the title compound, (I), in which, surprisingly, the dithiocarbamate ligand coordinates in a μ-η^1-η^1-mode.



(I)

The molecular structure of (I) shows a Re_2 unit which is doubly bridged by a μ-PCy_2 group and the dithiocarbamate ligand. Each Re atom is additionally attached to four terminal CO ligands and attains thus a slightly distorted octahedral coordination. Carbonyl groups 4 and 7, which are both in *trans*-position to the Re—P bonds, show ecliptic arrangement along the Re$\cdots$Re vector with a C—Re$\cdots$Re—C torsion angle of −1.6 (11)°, but the remaining CO ligands are staggered with torsion angles in the range 39.0 (5)–51.4 (6)°. The clearly non-bonding Re$\cdots$Re distance of 4.368 (1) Å is bridged by the $S_2C(9)NEt_2$ ligand, with an S$\cdots$S bite distance of 3.048 (4) Å. The accompanying S—C—S angle is 123.1 (7)° and the S—Re$\cdots$Re—S torsion angle of 57.8 (1)° shows the molecule to be twisted along the C9$\cdots$P vector. The S_2CN group itself is planar and forms a dihedral angle of 47.3 (2)° with the Re_2P plane. The μ-P bridge is symmetric with equal Re—P bond lengths of 2.562 (3) and 2.561 (3) Å, whereas the two Re—S bonds of 2.531 (3) and 2.485 (3) Å differ significantly. Similar patterns of likewise bridging dithio ligands are known for $(Et_4N)[Re_2(\mu\text{-}S)_2(\mu\text{-}S_2)(\mu\text{-}S_2COR)(S_2COR)_2]$ (McConnachie & Stiefel, 1999) and $Re_2(CO)_8(\mu\text{-}S_2CPCy_3)$ (Alvarez *et al.*, 1991), both with direct Re—Re bonds. The related Re—S bond lengths for these two compounds, of 2.442 (2)/2.462 (1) Å and 2.462 (5)/2.518 (5) Å, respectively, are somewhat shorter than those for (I). The first structure exhibits Re^{IV} atoms with strongly distorted octahedral S_6 coordination spheres and a completely planar $Re_2\mu$-S_2CO fragment. For the second structure the same twisted $M_2\mu$-S_2C geometry is observed as for (I), for $Os_2N[S_2CN(CH_3)_2]_5$ (Given & Pignolet, 1977) and for $Ru_2(CO)_4(\mu$-$S_2CH)(\mu$-$PBu_2)(\mu$-dppm) (Böttcher *et al.*, 2000) as well. S⋯S bite distances of these other structures range from 3.02 to 3.15 Å and the S—C—S angles from 128.7 to 130.7°.

Experimental

In a Schlenk tube, 150 mg (0.172 mmol) $Re_2(\mu$-Br$)(\mu$-$PCy_2)(CO)_8$ was dissolved in 20 ml THF. 39 mg (0.228 mmol) NaS_2CNEt_2 was added and the reaction mixture was stirred for 24 h. The solvent was removed and the resulting residue subjected to TLC (eluent: dichloromethane/hexane, 1:10). From the major band, a pale yellow substance was isolated which, upon recrystallization from dichloromethane/pentane, gave 75 mg (46% yield) of the title compound. Spectroscopic data: ν(CO)–IR: 2090 (*vw*), 2077 (*s*), 1998 (*vs*), 1936 (*s*). ^{1}H NMR ($CDCl_3$): 1.23–2.34 (*m*, 28H; Cy, Me), 4.18 (*q*, $^3J_{HH}$ = 6.8 Hz, 4H, NCH_2). ^{13}C NMR ($CDCl_3$): 13.0 (*s*, Me), 26.0 [*s*, C^4(Cy)], 27.5 [*d*, $^2J_{CP}$ = 9 Hz, C^2(Cy)], 33.2 [*s*, C^3(Cy)], 41.0 [*d*, $^1J_{CP}$ = 11 Hz, C^1(Cy)], 51.2 (*s*, NCH_2), 183.5 [*d*, $^2J_{CP}$ = 40 Hz, CO (*trans* μ-P)], 188.6 (*d*, $^2J_{CP}$ = 6 Hz, CO); 190.2 (*d*, $^2J_{CP}$ = 7 Hz, CO), 208.7 (*s*, S_2CN). ^{31}P NMR ($CDCl_3$): 22.5 (*s*, μ-P).

Crystal data

$[Re_2(C_5H_{10}NS_2)(C_{12}H_{22}P)(CO)_8]$
$M_r = 942.01$
Triclinic, $P\overline{1}$
$a = 9.218$ (2) Å
$b = 11.891$ (2) Å
$c = 14.624$ (2) Å
$\alpha = 96.40$ (1)°
$\beta = 99.89$ (2)°
$\gamma = 102.06$ (2)°
$V = 1526.1$ (5) Å^3

$Z = 2$
$D_x = 2.050$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7.3$–15.6°
$\mu = 8.16$ mm^{-1}
$T = 203$ (2) K
Block, colorless
0.30 × 0.26 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.121$, $T_{max} = 0.187$
8235 measured reflections
6945 independent reflections
5125 reflections with $I > 2\sigma(I)$

$R_{int} = 0.053$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 1$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 19$
3 standard reflections every 397 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.149$
$S = 1.05$
6945 reflections
353 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 15.7996P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.25$ e Å^{-3}
$\Delta\rho_{min} = -1.04$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0038 (4)

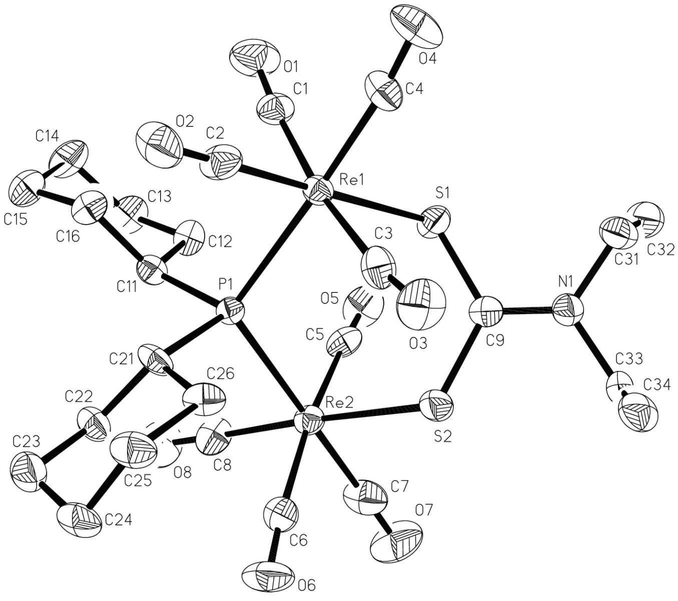


Figure 1
The molecular structure of (I) with H atoms omitted. Displacement ellipsoids are drawn at the 50% probability level.

Table 1
Selected geometric parameters (Å, °).

Re1—S1	2.531 (3)	Re2—P1	2.562 (3)
Re1—P1	2.561 (3)	S1—C9	1.740 (12)
Re2—S2	2.485 (3)	S2—C9	1.727 (12)
S1—Re1—P1	91.58 (10)	Re1—P1—Re2	117.03 (11)
S2—Re2—P1	91.86 (10)	N1—C9—S2	118.0 (9)
C9—S1—Re1	108.5 (4)	N1—C9—S1	118.9 (9)
C9—S2—Re2	114.9 (4)	S2—C9—S1	123.1 (7)

H atoms were placed at calculated positions, riding on the attached C atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C)$ for methyl groups. Residual electron density of 1.25 e Å^3 is found at (0.058, 0.871, 0.327), 0.96 Å from Re1.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Acta Cryst. (2002). E**58**, m116–m117 Hans Egold *et al.* • $[Re_2(C_5H_{10}NS_2)(C_{12}H_{22}P)(CO)_8]$ **m117**