Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Sulfido-bridged rhenium–carbonyl complexes with planar and folded Re_2S_2 cores

Ulrich Flörke,* Hans Egold and Detlev Schwarze

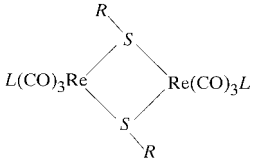
Fachbereich Chemie und Chemietechnik, Universität-GH Paderborn, Warburgerstr. 100, D-33098 Paderborn, Germany
Correspondence e-mail: uf@chemie.uni-paderborn.de

Received 11 November 1999
Accepted 23 November 1999

The two sulfido-bridged dirhenium complexes bis(μ-4-methoxyphenylsulfido-*S*)bis(tetracarbonylrhenium), [$Re_2(C_7H_7OS)_2(CO)_8$], and bis(μ-naphthylsulfido-*S*)bis[tricarbonyl(dicyclohexylphosphane)rhenium], [$Re_2(C_{12}H_{23}P)_2(C_{10}H_7S)_2(CO)_6$], show different geometries of the common Re_2S_2 core. The 4-methoxyphenyl derivative has crystallographic $\bar{1}$ symmetry and the naphthyl derivative has C^2 symmetry. This results from intramolecular repulsion due to different substitution patterns at the Re and S atoms.

Comment

We reported recently new synthetic routes to hydrido sulfido-bridged dirhenium complexes (Egold *et al.*, 1999). In this context, the new doubly sulfido-bridged complexes $Re_2(\mu\text{-}SR)_2(CO)_8$, (I) ($R$ = 4-methoxyphenyl), and $Re_2(\mu\text{-}SR')_2(CO)_6(PHCy_2)_2$, (II) ($R'$ = naphthyl; Cy = cyclohexyl), were also prepared. These two compounds differ markedly in their molecular geometries.



(I) R = 4-methoxyphenyl; L = CO
(II) R = naphthyl; L = $PHCy_2$

In (I) (Fig. 1), each Re atom is octahedrally coordinated by two axially and two equatorially positioned carbonyl groups and two bridging S atoms. The CO groups show an ecliptic arrangement with torsion angles C4—Re···Re^i—$C3^i$ and C2—Re···Re^i—$C1^i$ of 0.4 (3) and 1.3 (3)°, respectively [symmetry code: (i) $-1-x, 1-y, -z$). The geometric centre of the molecule lies on a crystallographic inversion centre. Consequently, the Re_2S_2 core is planar and the methoxyphenyl groups attached to the μ-S atoms adopt *anti* positions. The two Re—S bond lengths of 2.524 (1) and 2.518 (1) Å differ only slightly, but they are significantly elongated

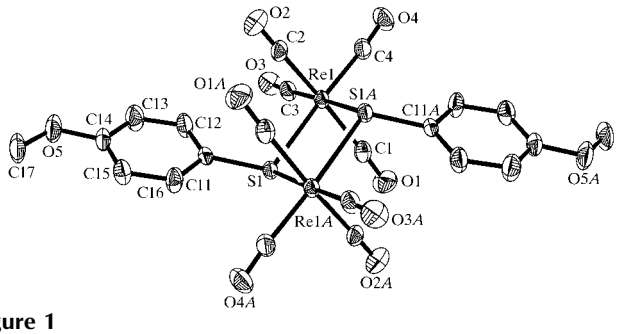


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

compared with those of 2.471 (3) or 2.478 (3) Å, respectively, found in the hydrido sulfido-bridged complexes $Re_2(\mu\text{-H})(\mu\text{-}SR)(CO)_8$ (R = phenyl or naphthyl; Egold *et al.*, 1999). The related acetonitrile-substituted complex $Re_2(\mu\text{-}S^tBu)_2(CO)_6(CH_3CN)_2$ (Eremenko *et al.*, 1992) exhibits Re—S bond lengths of 2.522 (2) and 2.534 (2) Å. The enclosed ring angles of (I) are Re—S—Re 98.47 (4)° and S—Re—S 81.53 (4)°, and the non-bonding Re···Re separation is 3.819 (1) Å. The basic structural elements of (I), the planar M_2S_2 ring and the *anti* position of the R residues at the sulfido bridges, are also valid for the above-mentioned rhenium acetonitrile complex, for the complex $Re_2(\mu\text{-}SR)_2(CO)_8$ [R = $CS_2Re(CO)_4$] (Thiele *et al.*, 1974) as well as for the two manganese compounds $Mn_2(\mu\text{-S-phenyl})_2(CO)_8$ (Onaka & Katukawa, 1996) and $Mn_2(\mu\text{-S-tolyl})_2(CO)_8$ (Chen *et al.*, 1996).

In contrast to this, the core structure of (II) (Fig. 2) is entirely different showing a folded Re_2S_2 ring with an Re_2S/SRe_2 dihedral angle of 137.8 (1)° and naphthyl residues at both bridging S atoms in the *syn* position. The coordination of Re by the two μ-S atoms, three CO groups and one axially attached $PHCy_2$ ligand is slightly distorted octahedral. These latter terminal ligands show a largely ecliptic arrangement with torsion angles of 6.4 (7)° for C3—Re···Re^{ii}—$C1^{ii}$, 9.2 (1)° for P1—Re···Re^{ii}—$P1^{ii}$ and 10.3 (7)° for C2—Re···Re^{ii}—$C2^{ii}$ [symmetry code: (ii) $-x, y, \frac{1}{2}-z$). The phos-

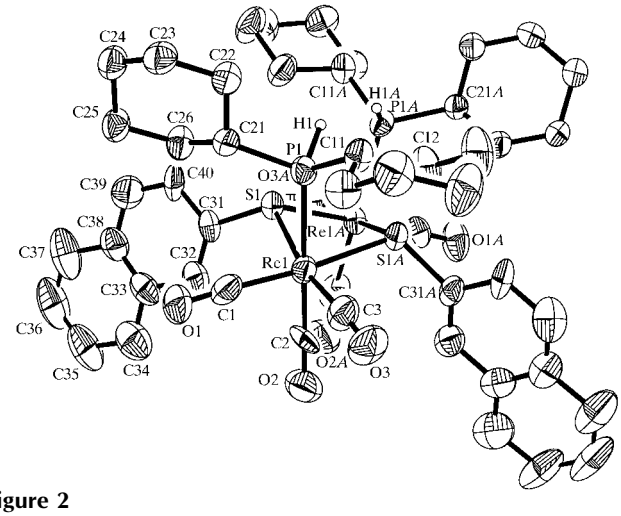


Figure 2
The molecular structure of (II) showing 50% probability displacement ellipsoids. Cyclohexyl- and naphthyl-H atoms have been omitted for clarity.

phido ligands at the Re atoms are in the *syn* position too, and a crystallographic twofold axis runs through the midpoint of the Re···Re vector. This geometry results in the axial $PHCy_2$ and CO ligands having intramolecular non-bonding distances of PH···HP 2.32 (15) Å [P—H is 1.44 (8) Å] and O···O 2.994 (15) Å. For a corresponding planar molecule like (I), the carbonyl O···O distances are about 3.2 Å, but the calculated PH···HP separation of 0.9 Å and cyclohexyl CH···HC separation of 1.8 Å would clearly be too short and the resulting repulsive forces give rise to the observed ring distortion. Similar ring folding in order to reduce intramolecular repulsion is also known for μ-P-bridged complexes (Flörke & Haupt, 1994). The Re—S bond lengths of 2.523 (2) and 2.526 (2) Å compare well with those of (I), but the Re—S—Re and S—Re—S angles of 98.93 (8) and 74.64 (8)°, respectively, reflect the folding of the ring. The non-bonding Re···Re distance is 3.838 (1) Å.

Experimental

For the preparation of (I), $Re_2(CO)_{10}$ (200 mg, 0.307 mmol) and 4-methoxy-thiophenol (75 µl, 0.612 mmol) were heated at 443 K in a sealed glass tube in the presence of xylene (1.5 ml) for 10 h. Subsequent thin-layer chromatography (TLC) separation (eluant: dichloromethane/*n*-hexane 1/5) gave (I) in 10% yield. Single crystals were grown from chloroform/*n*-pentane. For the preparation of (II), trimethylamine *N*-oxide (17 mg, 0.226 mmol) were added to a solution of $Re_2[\mu$-S(2-naphthyl)$]_2(CO)_8$ (100 mg, 0.109 mmol) and $PHCy_2$ (44 µl, 0.218 mmol) in tetrahydrofuran. The Re adduct was prepared according to Treichel & Tegen (1988). After stirring for 2 h, (II) was isolated by TLC separation (eluant: dichloromethane/*n*-hexane 1/2) in 60% yield. Single crystals were grown from dichloromethane/*n*-pentane.

Compound (I)

Crystal data

$[Re_2(C_7H_7OS)_2(CO)_8]$
M_r = 874.85
Monoclinic, $P2_1/n$
a = 9.731 (2) Å
b = 9.638 (1) Å
c = 13.772 (1) Å
β = 107.66 (1)°
V = 1230.8 (3) Å^3
Z = 2
D_x = 2.361 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
θ = 7.323–22.046°
μ = 10.051 mm^{-1}
T = 203 (2) K
Block, pale yellow
0.44 × 0.24 × 0.18 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.080, T_{max} = 0.164
3716 measured reflections
2832 independent reflections
2448 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 27.50°
$h = -12 \rightarrow 1$
$k = -1 \rightarrow 12$
$l = -17 \rightarrow 17$
3 standard reflections every 397 reflections
intensity decay: < 1%

Table 1
Selected geometric parameters (Å, °) for (I).

Re1—S1^i	2.5179 (12)	S1—C11	1.796 (4)
Re1—S1	2.5243 (12)		
S1^i—Re1—S1	81.53 (4)	C11—S1—Re1	114.20 (16)
C11—S1—Re1^i	111.92 (16)	Re1^i—S1—Re1	98.47 (4)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.063
S = 1.049
2832 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 1.1289P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.991 e Å^{-3}
$\Delta\rho_{min}$ = −0.995 e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1995*a*)
Extinction coefficient: 0.00201 (18)

Compound (II)

Crystal data

$[Re_2(C_{12}H_{23}P)_2(C_{10}H_7S)_2(CO)_6]$
M_r = 1255.44
Monoclinic, $C2/c$
a = 24.561 (3) Å
b = 9.378 (3) Å
c = 23.722 (3) Å
β = 112.63 (1)°
V = 5043.3 (18) Å^3
Z = 4
D_x = 1.653 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 35 reflections
θ = 8.705–15.577°
μ = 4.988 mm^{-1}
T = 293 (2) K
Prism, colourless
0.41 × 0.10 × 0.08 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.482, T_{max} = 0.671
6948 measured reflections
5783 independent reflections
2766 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 27.50°
$h = -31 \rightarrow 1$
$k = -1 \rightarrow 12$
$l = -28 \rightarrow 30$
3 standard reflections every 397 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.117
S = 1.021
5783 reflections
284 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2 + 11.0195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$ = 0.991 e Å^{-3}
$\Delta\rho_{min}$ = −0.501 e Å^{-3}
Extinction correction: *SHELXTL* (Siemens, 1995*a*)
Extinction coefficient: 0.00016 (3)

Table 2
Selected geometric parameters (Å, °) for (II).

Re1—P1	2.484 (3)	Re1—S1	2.526 (2)
Re1—S1^i	2.523 (2)	S1—C31	1.780 (10)
S1^i—Re1—S1	74.64 (8)	C31—S1—Re1	115.7 (3)
C31—S1—Re1^i	110.4 (3)	Re1^i—S1—Re1	98.93 (8)

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

In (II), H1 on P1 was refined isotropically [P1—H1 1.44 (8) Å], while all other H atoms were constrained and treated as riding atoms.

For both compounds, data collection: *XSCANS* (Siemens, 1995*b*); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Siemens, 1995*a*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1446). Services for accessing these data are described at the back of the journal.

References

Chen, J., Young, V. G. & Angelici, R. J. (1996). *Organometallics*, **15**, 325–331.

Egold, H., Schwarze, D. & Flörke, U. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3203–3207.

Eremenko, I. L., Pasynskii, A. A., Nefedov, S. E., Katugin, A. S., Kolobkov, B. I., Shaposhnikova, A. D., Stadnichenko, R. A., Yanovskii, A. I. & Struchkov, Yu. T. (1992). *Russ. J. Inorg. Chem.* **37**, 284–289.

Flörke, U. & Haupt, H.-J. (1994). *Acta Cryst.* C**50**, 378–380.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Onaka, S. & Katukawa, Y. (1996). *J. Coord. Chem.* **39**, 135–146.

Siemens (1995*a*). *SHELXTL*. Version 5.10. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995*b*). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Thiele, G., Liehr, G. & Lindner, E. (1974). *J. Organomet. Chem.* **70**, 427–435.

Treichel, P. M. & Tegen, M. H. (1988). *J. Organomet. Chem.* **358**, 339–345.