PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 1659–1664

POLYHEDRON

www.elsevier.com/locate/poly

Photochemical reactions of $Re(CO)_5Br$ with tetraalkyldiphosphine disulfides (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph) and the crystal structure of $[ReBr(CO)_3(Et_2P(S)P(S)Et_2)]$

Ozan Sanlı Şentürk [a,b,*], Hawry A. Shekhel [a], Brian T. Sterenberg [b], Konantin A. Udachin [b], Sema Sert [a], Ümmühan Özdemir [c], Fadime Uğur Sarikahya [a]

[a] Department of Chemistry, Faculty of Science, Ege University, Bomova, 35100 Izmir, Turkey
[b] Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ont., Canada K1A 0R6
[c] Department of Chemistry, Faculty of Science and Literature, Gazi University, Teknikokullar, 06500 Ankara, Turkey

Received 24 August 2002; accepted 15 April 2003

Abstract

The hitherto unknown series of complexes *fac*-$[Re(CO)_3Br\{R_2P(S)P(S)R_2\}]$ **1a**–**5a** (**1a**, R = Me; **2a**, R = Et; **3a**, R = ^{n}Pr; **4a**, R = ^{n}Bu; **5a**, R = Ph) and $[Re_2(CO)_8Br_2\{cis\text{-}\mu\text{-}R_2P(S)P(S)R_2\}]$ **1b**–**5b** [**1b**, R = Me; **2b**, R = Et; **3b**, R = ^{n}Pr; **4b**, R = ^{n}Bu; **5b**, R = Ph] have been prepared by the photochemical reaction of $Re(CO)_5Br$ with $R_2P(S)P(S)R_2$. The complexes have been characterized by elemental analysis, mass spectroscopy (EI), FT-IR and $^{31}P\{^1H\}$ NMR spectrometry. The spectroscopic studies suggest *cis*-chelate bidentate coordination of the ligand in *fac*-$[Re(CO)_3Br\{R_2P(S)P(S)R_2\}]$ and *cis*-bridging bidentate coordination of the ligand between two metals in $[Re_2(CO)_8Br_2\{cis\text{-}\mu\text{-}R_2P(S)P(S)R_2\}]$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph). An X-ray diffraction study of $[ReBr(CO)_3(Et_2P(S)P(S)Et_2)]$ confirms that the rhenium adopts a distorted octahedral geometry with local C_s symmetry.

Keywords: Diphosphine disulfide

1. Introduction

Since the preparation of the first tetraalkyldiphosphine disulfides complexes in 1965 [1–7] such compounds have continued to attract attention, in part because of the different possible coordination geometries which the ligand may adopt. We have recently discovered a photochemical reaction of $M(CO)_6$ (M = Mo, W) with $R_2P(S)P(S)R_2$ (R = Me, Et, ^{n}Pr, ^{n}Bu) to give the chelate complexes $[M(CO)_4\{R_2P(S)P(S)R_2\}]$ (R = Me, Et, ^{n}Pr, ^{n}Bu) [8], where the ligand is presumed to adopt the expected *cis*-chelate bidentate coordination. However, in certain cases, the ligand bridges between two metals affording $[M_2(CO)_{10}\{\mu\text{-}R_2P(S)P(S)R_2\}]$ (R = Me, Et, ^{n}Pr, ^{n}Bu) [9] as secondary products.

Both product types detailed above the tetraalkyldiphosphine disulfides remain intact. This is not always the case and in certain reactions fragmentation has been observed. For example, the formation of, inter alia, $[Me_2PS_2]$ ions has been reported upon reaction of OH with $Me_2P(S)P(S)Me_2$ in the chemical ionization source of a mass spectrometer [10]. The reaction of $Co_2(CO)_8$ and $Me_2P(S)P(S)Me_2$ was first described in 1972 and two clusters were reported [11], while later the X-ray crystal structure of one of these, namely $[Co_4(CO)_9(\mu_3\text{-}S)(\mu\text{-}PMe_2)]$ confirmed that both phosphorus–sulfur and phosphorus–phosphorus scission had occurred [12,13].

In this paper, we report the preparation and characterization of new complexes *fac*-$[Re(CO)_3Br\{R_2P(S)P(S)R_2\}]$ and $[Re_2(CO)_8Br_2\{cis\text{-}\mu\text{-}R_2P(S)P(S)R_2\}]$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph), which were prepared by photochemical reactions between $Re(CO)_5Br$ with $Ph_2P(S)P(S)Ph_2$. The complexes were characterized by elemental analyses, mass spectroscopy (EI), FT-IR

---

* Corresponding author. Tel.: +1-613-990-5836.
E-mail address: ozan.senturk@nrc.ca (O.S. Şentürk).

0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00327-9

and $^{31}P\{^{1}H\}$ NMR spectroscopy. The spectroscopic studies suggest *cis*-chelate bidentate coordination of the ligand in *fac*-[Re(CO)$_3$Br{R$_2$P(S)P(S)R$_2$}] and *cis*-bridging bidentate coordination of the ligand between two metals in [Re$_2$(CO)$_8$Br$_2${*cis*-μ-R$_2$P(S)P(S)R$_2$}] (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph). An X-ray diffraction study of [ReBr(CO)$_3$(Et$_2$P(S)P(S)Et$_2$)] confirms that the rhenium adopts a distorted octahedral geometry with local C_s symmetry.

2. Experimental

2.1. General

Reactions were carried out under dry nitrogen by using Schlenk techniques. All solvents were dried and degassed prior to use. Elemental analyses were carried out using a LECO-CHNS-O-9320 by Technical and Scientific Research Council of Turkey, TUBITAK. FT-IR spectra were recorded on samples in hexane at the Ege University on a Mattson 1000 FT spectrophotometer. $^{31}P\{^{1}H\}$ NMR spectra were recorded in CDCl$_3$/CD$_2$Cl$_2$ at UCL on a BRUKER DPX-400, 400 MHz High Performance Digital FT-NMR, TUBITAK. Electron Impact-Mass Spectra were recorded on Micromass VG Platform-II LC-MS at TUBITAK. UV irradiations were performed with a medium-pressure 400 W mercury lamp through a quartz-walled immersion well reactor. Pentane, benzene, hexane, dichloromethane, acetone and silica gel were purchased from Merck, and Re(CO)$_5$Br was purchased from Aldrich. These reagents were used as supplied. The tetraaalkyldiphosphine disulfides R$_2$P(S)P(S)R$_2$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph) were prepared by literature methods [14,15].

2.2. Synthesis

The complexes, *fac*-[Re(CO)$_3$Br{R$_2$P(S)P(S)R$_2$}], **1a**–**5a**, and [Re$_2$(CO)$_8$Br$_2${*cis*-μ-R$_2$P(S)P(S)R$_2$}], **1b**–**5b**, were prepared by the photochemical reactions of Re(CO)$_5$Br with R$_2$P(S)P(S)R$_2$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph) and obtained in 40–60% yield by similar methods of which the following is typical.

The complexes Re(CO)$_5$Br (0.8 g, 2 mmol) and Me$_2$P(S)P(S)Me$_2$ (0.18 g, 1 mmol) were dissolved in tetrahydrofuran (80–100 ml) and the solution was irradiated for 2 h using a 400-W medium-pressure mercury lamp through a quartz-walled immersion well reactor. During the irradiation, the colour of the solution changed from colourless to dark yellow. After the irradiation the solvent was evaporated under the vacuum resulting in a dark yellow solid which was extracted into dichloromethane (10 ml). Addition of petroleum ether (50 ml) resulted in precipitation of a dark yellow solid which was washed with petroleum ether and dried under vacuum, and shown to be *fac*-[Re(CO)$_3$Br{Me$_2$P(S)P(S)Me$_2$}] (**1a**) (42% yield). The yellow solution was evaporated and the residue separated chromatographically through a column packed with silica gel using *n*-pentane as an eluant. A yellow fraction was isolated and dried in vacuo to give [Re$_2$(CO)$_8$Br$_2${*cis*-μ-Me$_2$P(S)P(S)Me$_2$}] (**1b**) (39% yield).

2.3. *1a*

ReC$_7$H$_{12}$O$_3$P$_2$S$_2$Br, (MW = 536), Calc.: C, 15.7; H, 2.3; S, 11.9. Found: C, 15.9; H, 2.7; S, 12.0%. IR (KBr), ν(CO): 2022(s), 1934(s), 1901(s) cm^{-1}; ν_{sym}(PS): 580 cm^{-1}; ν_{as}(PS): 542 cm^{-1}; $^{31}P\{^{1}H\}$ NMR (100 MHz CD$_2$Cl$_2$) δ_P: 54.7 ppm. MS (EI, 70 eV), *m/z* (%): 532.63 (6.25), [M^+–(4H)]; 322 (7.25), [M^+–(tmps+CO)]; 294 (12.50), [M^+–(tmps+2CO)]; 266 (40.2), [M^+–(tmps+3CO)]; 186 (18.06), [M^+–(3CO+Br)].

2.4. *2a*

ReC$_{11}$H$_{20}$O$_3$P$_2$S$_2$Br, (MW = 592), Calc.: C, 22.3; H, 3.4; S, 10.8. Found: C, 22.5; H, 3.7; S, 10.9%. IR (KBr), ν(CO): 2019(s), 1919(s), 1898(s) cm^{-1}; ν_{sym}(PS): 577 cm^{-1}; ν_{as}(PS): 535 cm^{-1}; $^{31}P\{^{1}H\}$ NMR (100 MHz CD$_2$Cl$_2$) δ_P: 70.6 ppm. MS (EI, 70 eV), *m/z* (%): 242.06 (51.67), [M^+–(teps+Br+CO)]; 214.65 (6.07), [M^+–(teps+Br+2CO)]; 186.06 (12.26), [M^+–(teps+Br+3CO)].

2.5. *3a*

ReC$_{15}$H$_{28}$O$_3$P$_2$S$_2$Br, (MW = 648), Calc.: C, 27.8; H, 4.4; S, 9.9. Found: C, 28.0; H, 4.6; S, 10.1%. IR (KBr), ν(CO): 2018(s), 1912(s), 1893(s) cm^{-1}; ν_{sym}(PS): 595 cm^{-1}; ν_{as}(PS): 562 cm^{-1}; $^{31}P\{^{1}H\}$ NMR (100 MHz CD$_2$Cl$_2$) δ_P: 66.9 ppm. MS (EI, 70 eV), *m/z* (%): 540 (6), [M^+–(CO+Br)]; 149 (100), [Pr$_2$P(S)]; 106 (85), [PrP(S)]; 63 (45), [P(S)]; 512 (10), [M^+–(2CO+Br)]; 484 (6), [M^+–(3CO+Br)].

2.6. *4a*

ReC$_{19}$H$_{36}$O$_3$P$_2$S$_2$Br, (MW = 648), Calc.: C, 32.4; H, 5.2; S, 9.1. Found: C, 32.7; H, 5.3; S, 9.2%. IR (KBr), ν(CO): 2016(s), 1911(s), 1891(s) cm^{-1}; ν_{sym}(PS): 592 cm^{-1}; ν_{as}(PS): 565 cm^{-1}; $^{31}P\{^{1}H\}$ NMR (100 MHz CD$_2$Cl$_2$) δ_P: 67.3 ppm. MS (EI, 70 eV), *m/z* (%): 647 (5), [M^+–Bu]; 533 (20), [M^+–3Bu]; 476 (5), [M^+–4Bu]; 420 (4), [M^+–(4Bu+2CO)]; 392 (4), [M^+–(4Bu+3CO)]; 266 (13.74), [M^+–(tbps+CO)].

2.7. *5a*

$ReC_{27}H_{20}O_3P_2S_2Br$, (MW = 648), Calc.: C, 41.3; H, 2.6; S, 8.2. Found: C, 41.8; H, 2.9; S, 8.3%. IR (KBr), ν(CO): 2014(s), 1905(s), 1890(s) cm^{-1}; ν_{sym}(PS): 601 cm^{-1}; ν_{as}(PS): 582 cm^{-1}; $^{31}P\{^1H\}$ NMR (100 MHz CD_2Cl_2) δ_P: 63.5 ppm. MS (EI, 70 eV), *m*/*z* (%): 350 (8), [M^+−tPhps]; 322 (5), [M^+−(CO + tPhps)]; 294 (10), [M^+−(2CO + tPhps)]; 266 (20), [M^+−(3CO + tPhps)]; 186 (6.5), [M^+−(3CO + tPhps + Br)].

2.8. *1b*

$ReC_{12}H_{12}O_8P_2S_2Br$, (MW = 942), Calc.: C, 15.9; H, 1.8; S, 6.8. Found: C, 15.5; H, 1.6; S, 6.5%. IR (KBr), ν(CO): 2100(vs), 2011(s), 1922(s), 1899(s) cm^{-1}; ν_{sym}(PS): 588 cm^{-1}; ν_{as}(PS): 539 cm^{-1}; $^{31}P\{^1H\}$ NMR (100 MHz CD_2Cl_2) δ_P: 94.1 ppm. MS (EI, 70 eV), *m*/*z* (%): 521 (40), [M^+−(ReBr(CO)$_4$ + Me + CO)]; 493 (25), [M^+−(ReBr(CO)$_4$ + Me + 2CO)]; 465 (20), [M^+−(ReBr(CO)$_4$ + Me + 3CO)]; 437 (100), [M^+−(ReBr(CO)4 + Me + 4CO)].

2.9. *2b*

$ReC_{16}H_{20}O_8P_2S_2Br$, (MW = 998), Calc.: C, 19.2; H, 2.0; S, 6.4. Found: C, 19.9; H, 2.3; S, 6.9%. IR (KBr), ν(CO): 2101(vs), 2004(s), 1933(s), 1905(s) cm^{-1}; ν_{sym}(PS): 564 cm^{-1}; ν_{as}(PS): 524 cm^{-1}; $^{31}P\{^1H\}$ NMR (100 MHz CD_2Cl_2) δ_P: 91.1 ppm. MS (EI, 70 eV), *m*/*z* (%): 413 (10), [M^+−(ReBr(CO)$_4$ (Et)$_2$ PS) + 2Et + CO)]; 385 (20), [M^+−(ReBr(CO)$_4$ (Et)$_2$PS) + 2Et + 2CO)]; 357 (20) [M^+−(ReBr (CO)$_4$(Et)$_2$ PS) + 2Et + 3CO)]; 329 (25), [M^+−(ReBr(CO)$_4$(Et)$_2$PS) + 2Et + 4CO)].

2.10. *3b*

$ReC_{20}H_{28}O_8P_2S_2Br$, (MW = 1054), Calc.: C, 22.8; H, 2.7; S, 6.1. Found: C, 22.5; H, 2.9; S, 5.9%. IR (KBr), ν(CO): 2098(vs), 2015(s), 1932(s), 1898(s) cm^{-1}; ν_{sym}(PS): 589 cm^{-1}; ν_{as}(PS): 548 cm^{-1}; $^{31}P\{^1H\}$ NMR (100 MHz CD_2Cl_2) δ_P: 87.3 ppm. MS (EI, 70 eV), *m*/*z* (%): 530 (30), [M^+−(ReBr(CO)$_4$ + 2Pr + S + CO)]; 502 (16), [M^+−(ReBr(CO)$_4$ + 2Pr + S + 2CO)]; 474 (10), [M^+−(ReBr(CO)$_4$ + 2Pr + S + 3CO)]; 446 (100), [M^+−(ReBr(CO)$_4$ + 2Pr + S + 4CO)].

2.11. *4b*

$ReC_{24}H_{36}O_8P_2S_2Br$, (MW = 1010), Calc.: C, 25.9; H, 3.3; S, 5.8. Found: C, 25.7; H, 3.5; S, 5.4%. IR (KBr), ν(CO) 2102(vs), 2010(s), 1929(s), 1897(s) cm^{-1}; ν_{sym}(PS) 590 cm^{-1}; ν_{as}(PS) 549 cm^{-1}; $^{31}P\{^1H\}$ NMR (100 MHz CD_2Cl_2) δ_P: 88.2 ppm. MS (EI, 70 eV), *m*/*z* (%): 615 (10), [M^+−(ReBr(CO)$_4$ + Bu + S + CO)]; 587 (10), [M^+−ReBr(CO)$_4$ + Bu + S + 2CO)]; 559 (15), [M^+−ReBr(CO)$_4$ + Bu + S + 3CO)]; 531 (15), [M^+−ReBr(CO)$_4$ + Bu + S + 4CO)].

2.12. *5b*

$ReC_{32}H_{20}O_8P_2S_2Br$, (MW = 1190), Calc.: C, 32.3; H, 1.7; S, 5.4. Found: C, 32.5; H, 1.9; S, 5.6%. IR (KBr), ν(CO) 2102(vs), 2015(s), 1933(s), 1908(s) cm^{-1}; ν_{sym}(PS) 613 cm^{-1}; ν_{as}(PS) 571 cm^{-1}; $^{31}P\{^1H\}$ NMR (100 MHz CD_2Cl_2) δ_P: 84.3 ppm. MS (EI, 70 eV), *m*/*z* (%): 490 (90), [M^+−(ReBr(CO)$_4$(Ph)$_2$PS) + Ph + CO)]; 462 (30), [M^+−(ReBr(CO)$_4$(Ph)$_2$PS) + Ph + 2CO)]; 434 (30), [M^+−((ReBr(CO)$_4$(Ph)$_2$PS) + Ph + 3CO)].

For the mass spectral data relative intensities are given in parentheses; probable assignments in square brackets. For all assignments the most abundant isotopes of Re has been selected (^{187}Re, 62.9% abundant).

2.13. *Crystallography*

A single crystal of **2a** was mounted on a glass fibre. Diffraction measurements were made on a Siemens SMART CCD automatic diffractometer using graphite-monochromated Mo Kα radiation. The unit cell was determined from randomly selected reflections obtained using the SMART CCD automatic search, center index and least-squares routines. Crystal data and collection parameters are listed in Table 1. Integration was carried out using the program SAINT and an absorption correction was performed using SADABS. Structure solution was carried out using the SHELXTL 5.1 suite of programs. The space group $P2_1/n$ was chosen based upon systematic absences. The initial solution was obtained by direct methods and refined by successive least-squares cycles.

3. Result and discussion

The photogeneration of M(CO)$_5$ from M(CO)$_6$ (M = Cr, Mo or W) has been extensively studied. These 16-electron M(CO)$_5$ fragments react avidly with any available donor to form M(CO)$_5$L species, and where L is a chelating bidentate ligand, rapid continuation to the chelating M(CO)$_4$L or bridging M$_2$(CO)$_{10}$(μ-L) products may occur [8,9,16]. The photochemical reactions of Re(CO)$_5$Br with $R_2P(S)P(S)R_2$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph) proceed in this expected manner to yield the hitherto unknown series of complexes **1a**–**5a** and **1b**–**5b**.

The IR spectra data for **1a**–**5a** and **1b**–**5b** show a decrease in ν_{as}(PS) on coordination. In the free ligand the IR active mode ν_{as}(PS) is at 569 cm^{-1} for tetramethyldiphosphine disulfide [8,9,17]. On *cis*-chelate coordination two bands are observed: at ca. 580 cm^{-1}

Table 1
Crystal data and structure refinement of **2a**

Empirical formula	$C_{11}H_{20}BrO_3P_2ReS_2$
Formula weight	592.44
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	9.2966(9)
b (Å)	19.221(2)
c (Å)	10.637(1)
α (°)	90.00
β (°)	104.125(2)
γ (°)	90.00
V (Å^3)	1843.2(3)
Z	4
D_{calc} (Mg m^{-3})	2.135
Absorption coefficient (mm^{-1})	9.162
$F(0\,0\,0)$	1128
θ Range for data collection (°)	2.12–28.74
Limiting indices	$-12 \le h \le 12$, $-26 \le k \le 25$, $-14 \le l \le 14$
Reflections collected	21526
Independent reflections	4767
Completeness to θ	99.5
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	4767/0/181
Goodness-of-fit on F^2	1.067
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0642$, $wR_2 = 0.1342$
R indices (all data)	$R_1 = 0.0510$, $wR_2 = 0.1251$
Largest difference peak and hole (e Å^{-3})	6.276 and −3.275

ν_{sym}(PS) and ca. 542 cm^{-1} ν_{as}(PS), e.g. in $[Re(CO)_3Br\{Me_2P(S)P(S)Me_2\}]$ (**1a**). On *cis*-bridging coordination two bands are observed: at ca. 588 cm^{-1} ν_{sym}(PS) and ca. 539 cm^{-1} ν_{as}(PS) e.g. in $[Re_2(CO)_8Br_2\{cis\text{-}\mu\text{-}Me_2P(S)P(S)Me_2\}]$ (**1b**). The infrared spectra of the $[Re(CO)_3BrL\text{-}L]$ compounds are consistent with a structure in which L–L are *cis* to the Br as well as to each other. The infrared spectra for the complexes contain three strong carbonyl bands allowing an unequivocal assignment of $[Re(CO)_3BrL\text{–}L]$ compounds as the *fac*-isomer of C_s symmetry. The symmetry of these complexes *fac*-$[Re(CO)_3Br\{R_2P(S)P(S)R_2\}]$(R = Me, Et, ^{n}Pr, ^{n}Bu, Ph) is C_s. The three carbonyl stretching vibrations being distributed amongst the symmetry classes of the point group as follows ($\tau = 2A'' + A'$) [19]. The infrared spectra of the $[Re_2(CO)_8Br_2\{cis\text{-}\mu\text{-}L\text{–}L\}]$ compounds are consistent with a structure in which L–L are *cis* to the Br. As expected, four bands arising from ν(CO) vibrations are seen for each complex **1b**–**5b** which presumably have local C_{2v} symmetry of the $M(CO)_4$ unit in $[Re_2(CO)_8Br_2\{cis\text{-}\mu\text{-}R_2P(S)P(S)R_2\}]$(R = Me, Et, ^{n}Pr, ^{n}Bu, Ph). The IR spectroscopic results are in accord with a *cis*-chelating and a *cis*-bridging coordination ligand. The ν(CO) modes of **1a**–**5a** and **1b**–**5b** move to lower wave numbers when compared with the starting $Re(CO)_5Br$ molecules [8,9] (Fig. 1).

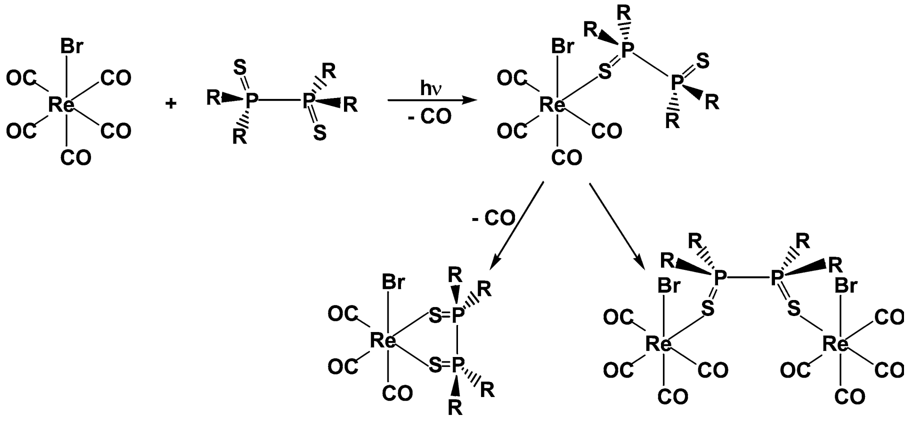
The $^{31}P\{^1H\}$ NMR spectra of complexes, **1a**–**5a** and **1b**–**5b**, show one signal corresponding to the phosphorus atoms of the coordinated ligands. The δ_P values of the coordinated ligands are at higher field than those of free ligands and the coordinated *cis*-bridging ligands are also at higher field than when the ligands are coordinated in a *cis*-chelating mode. Only one signal is observed in accord with the symmetry of the complexes [8,9,18].

The mass spectra show fragmentation via successive loss of CO groups and fragmentation of the organic ligands.

Single crystals of $[ReBr(CO)_3(Et_2P(S)P(S)Et_2)]$ (**2a**), were grown by slow diffusion of hexanes into a CH_2Cl_2 solution and an ORTEP diagram of the molecule is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. X-ray diffraction of **2a** shows that the tetraethyldiphosphine disulfides group adopts a chelating bidentate mode of ligation. The sulfur atoms of the tetraethyldiphosphine disulfides are bonded *trans* to CO groups, with the remaining CO group and the Br group occupying axial sites. The rhenium atom is thus six-coordinate with a somewhat distorted octahedral arrangement of the coordinating atoms. The Re–S (2.555(2) and 2.6154(8) Å) and P–S (1.996(2) and 1.990(2) Å) distance are in line with those observed for related complexes. For example, in the molecules $[Re(CO)_3(Et_4\text{-}DTO)Br]$ (**A**), and $[ReNCl\{N(SPPh_2)_2\text{-}S,S'\}(PPh_3)]$ (**B**), the average Re–S distance 2.473 Å [25,26] and in the molecule $[Rh(CO\text{-}D)(Et_2P(S)P(S)Et_2]ClO_4$ (**C**), the average P–S distance 2.001 Å [18]. The somewhat longer metal–sulfur and rather shorter P–S distances in **2a** presumably reflect somewhat weaker coordination of the sulfur ligand in **2a**. The P–S distances in **2a** are intermediate between those associated with formal single (2.122(1) Å) [20] and double (range 1.923(5)–1.966(2) Å) phosphorus sulfur bonds [21]. This finding suggests some of the delocalization of electrons and observed that the two P–S distances in **2a** are identical within the limits of experimental uncertainty [24].

The lengthening of the P–S bond upon coordination from the value observed in the free ligand (v. 1.94(1) Å) [22] is probably due to the lower electronic density available at the sulfur atom after its coordination to the metal center, and is reflected at the sulfur atom after its coordination to the metal center, and is reflected in the decrease in the decrease in the (P–S) IR band found in the region 580–530 cm^{-1}.

On the other hand, no significant change is observed for the P–P bond separation (2.213(2) Å) when compared with the value reported for the free tetraethyldiphosphine disulfides $Et_2P(S)(S)PEt_2$ (2.22(1) Å) [22]. Probably this bond is too far away from the metal to



1a – 5a

1b – 5b

Fig. 1. The photochemical reactions of $Re(CO)_5Br$ with $R_2P(S)P(S)R_2$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph).

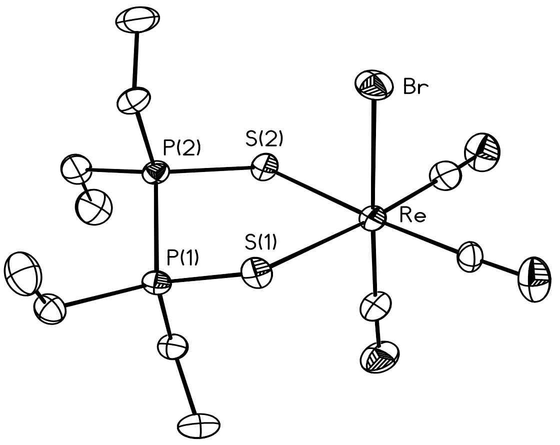


Fig. 2. Molecular structure of $[ReBr(CO)_3(Et_2P(S)P(S)Et_2)]$ (**2a**). Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms have been ommitted.

interact any appreciable modification upon coordination.

Table 2
Selected bond lengths (Å) and angles (°) for **2a**

Bond lengths			
Re–C(1)	1.908(7)	Re–S(1)	2.561(2)
Re–C(2)	1.906(7)	Re–S(2)	2.555(2)
Re–C(3)	1.881(7)	Re–Br	2.6514(8)
S(1)–P(1)	1.996(2)	P(1)–P(2)	2.213(2)
S(2)–P(2)	1.990(2)		
Bond angles			
C(3)–Re–C(2)	88.0(3)	S(2)–Re–S(1)	92.92(5)
C(3)–Re–C(1)	89.7(3)	C(1)–Re–Br	90.6(2)
C(2)–Re–C(1)	91.0(3)	C(3)–Re–Br	177.2(2)
C(3)–Re–S(2)	91.8(2)	C(2)–Re–Br	89.2(2)
C(2)–Re–S(2)	174.7(2)	S(1)–Re–Br	86.85(4)
C(1)–Re–S(2)	83.8(2)	S(2)–Re–Br	90.96(5)
C(3)–Re–S(1)	93.0(2)	S(1)–P(1)–Re	102.56(8)
C(2)–Re–S(1)	92.3(2)	S(2)–P(2)–Re	105.17(8)
C(1)–Re–S(1)	175.8(2)		

In addition, the values for the Re–S–P angles (102.56(8) and 105.17(8) (°)), close to tetrahedral, indicates formal sp^3 hybridization for sulfur, as reported for the related rhodium compound **C** [19]. These facts support the suggestion, that the phosphine–sulfides can be regarded as moderate σ-donor ligands with minimal π-acceptor properties [23].

We have presented the novel photochemical reactions between $Re(CO)_5Br$ and $R_2P(S)(P(S)R_2$ (R = Me, Et, ^{n}Pr, ^{n}Bu, Ph). The IR spectroscopic results are in accord with a *cis*-chelating **1a**–**5a** and a *cis*-bridging **1b**–**5b** bidentate coordination of the ligand [3]. The ν(CO) modes of **1b**–**5b** move to low wavenumber when compared with the starting $Re(CO)_5Br$ molecules. The ^{31}P NMR data show that the P atoms of the $R_4P_2S_2$ ligands are somewhat deshielded with respect to the free ligand. The mass spectrum shows fragmentation via successive loss of CO groups and fragmentation of the $R_2P(S)P(S)R_2$ ligand. In addition, the spectroscopic study of **2a** is entirely keeping with the single crystal X-ray diffraction study.

4. Supplementary material

A complete list of bond lengths and angles and tables of atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 190232. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank BP (Turkey) for the provision of photochemical apparatus and Research Foundation of Ege

University for funds. We thank TUBITAK for allocation of time at the NMR, Mass Spectra and Elemental Analyses. We thank Dr. Arthur J. Carty for allowing use of the X-ray facilities at the National Research Council of Canada.

References

[1] K. Baker, G.W.A. Fowles, J. Less Common Met. 8 (1965) 45.
[2] A.H. Cowley, Chem. Rev., 6 (1965) 65.
[3] D.W. Meek, P. Nicpon, J. Am. Chem. Soc. 87 (1965) 4951.
[4] F.A. Cotton, B.A. Franz, D.L. Hunter, Z.C. Mester, Inorg. Chim. Acta 11 (1974) 111.
[5] F.A. Cotton, B.A. Franz, D.L. Hunter, Z.C. Mester, Inorg. Chim. Acta 11 (1974) 119.
[6] K.P. Wagner, R.W. Hess, P.M. Treichel, J.C. Calabrese, Inorg. Chem. 14 (1975) 1121.
[7] H. Teichmann, Angew. Chem., Int. Ed. Engl. 4 (1965) 785.
[8] M.J. Almond, F. Sarikahya, O.S. Şentürk, Polyhedron 16 (1997) 1101.
[9] F. Sarikahya, O.S. Şentürk, Syn. React. Inorg. Met. 31 (1843) 2001.
[10] J. O'Hair, J.C. Sheldon, H.H. Bowie, J. Chem. Soc., Dalton Trans. (1988) 2837.
[11] G. Natile, S. Pignataro, G. Innorta, G. Bor, J. Organomet. Chem. 40 (1972) 955.
[12] G. Geraviso, F. Musso, S. Vastag, G. Bor, G. Szalantai, L. Marko, J. Clust. Sci. 5 (1994) 401.
[13] F. Sarikahya, O.S. Şentürk, I. Topaloğlu, Syn. React. Inorg. Met. 30 (2000) 1697.
[14] (a) T. Moeller, H.J. Birch, N.C. Nielson, Inorg. Synth. 4 (1953) 71;
(b) S.A. Butter, J. Chatt, Inorg. Synth. 15 (1974) 186;
(c) A.I. Vogel, Text-book of Practical Organic Chemistry, 3rd ed., Longman, London, 1977, pp. 139–145, 163–179, 193, 280–288.;
(d) H. Nierbergall, B. Langenfeld, Chem. Ber. 95 (1962) 64.
[15] P.J. Christen, L.M. Van der Linde, F.N. Hooge, Recl. Trav. Chim. 78 (1959) 161.
[16] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fifth ed., Wiley Interscience, New York, 1988, p. 1047.
[17] (a) G.P. McQuillan, I.A. Oxton, Spectrochim. Acta, Part A 33 (1977) 233;
(b) G.P. McQuillan, I.A. Oxton, Spectrochim. Acta, Part A 35 (1979) 865;
(c) G.P. McQuillan, I.A. Oxton, J. Chem. Soc., Dalton Trans. (1979) 895;
(d) A.H. Cowley, W.D. White, Spectrochim. Acta 22 (1966) 1431.
[18] C. Claver, A. Ruiz, M.A. Masdeu, J. Vinas, T. Saballs, F.J. Lahoz, F.J. Plou, Organomet. Chem. 373 (1989) 269.
[19] (a) U. Mazzi, A. Binmondo, N. Kotsev, D.A. Clemente, J. Organomet. Chem. 135 (1977) 177;
(b) R.H. Reiman, E. Singleton, J. Organomet. Chem. 59 (1973) 309.
[20] E. Fluc, G. Gonzalez, K. Peers, G.H. Von Schnerring, Z. Anorg. Allg. Chem. 473 (1981) 51.
[21] (a) A.K. Kerr, P.M. Boorman, B.S. Misener, G.A. Van Roode, Can. J. Chem. 55 (1977) 3081;
(b) T.S. Cameron, B. Dahlen, J. Chem. Soc., Perkin II (1975) 1737.
[22] S.N. Dutta, M.M. Woolfson, Acta Crystallogr. 14 (1961) 1514.
[23] E.W. Ainscough, A.M. Brodie, E. Mentzer, J. Chem. Soc., Dalton Trans. (1973) 2167.
[24] M.J. Almond, M.G.B. Drew, F. Sarikahya, O.S. Şentürk, Polyhedron 14 (1995) 1433.
[25] R. Rossi, A. Marchi, L. Marvelli, L. Magon, M. Peruzzini, U. Cesellato, R. Graziani, J. Chem. Soc., Dalton Trans. (1993) 723.
[26] P.C. Servaas, D.J. Stufkens, A. Oskam, P. Vernoojis, E.J. Baerends, D.J.A. De Ridder, C.H. Stam, Inorg. Chem. 28 (1989) 4104.