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Preparation and crystal structures of dirhenium face-sharing bioctahedral complexes $Re_2(\mu\text{-}SR)_3X_4(PR_3)_2$, R = methyl, ethyl or phenyl, and X = Cl or Br

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Abstract

The reactions of $Re_2Cl_4(PEt_2Ph)_4$, Et = ethyl and Ph = phenyl, with excess methyl disulfide (MeSSMe) and phenyl disulfide (PhSSPh) produce the compounds $Re_2(\mu\text{-}SMe)_3Cl_4(PEt_2Ph)_2$ (**1**) and $Re_2(\mu\text{-}SPh)_3Cl_4(PEt_2Ph)_2\cdot$acetone (**2**), respectively. Similarly, $Re_2Cl_5(PMePh_2)_3$ reacts with PhSSPh to yield $Re_2(\mu\text{-}SPh)_3Cl_4(PMePh_2)_2$ (**3**) and $Re_2Br_4(PEt_2Ph)_4$ reacts with either EtSSEt or PhSSPh to produce either $Re_2(\mu\text{-}SEt)_3Br_4(PEt_2Ph)_2$ (**4**) or $Re_2(\mu\text{-}SPh)_3Cl_4(PEt_2Ph)_2$ (**5**). All of these new Re_2^{7+} complexes display one-electron paramagnetism. X-ray crystallographic studies of compounds **1**–**4** reveal a common face-sharing bioctahedral structure with three bridging thiolate ligands. The Re–Re bond distances (averaging 2.473 Å) are indicative of multiple metal–metal bonds. Compound **1** may also be prepared in low yield by the reaction of $Re_2Cl_4(PEt_2Ph)_4$ with 2,5-dithiahexane or the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with a mixture of MeSSMe and PEt_2Ph.

Keywords: Dirhenium complexes; Metal–metal multiple bonds; Crystal structures; Face-sharing bioctahedral complexes; Thiolate ligands; Phosphine ligands

1. Introduction

Studies of the reactivity of dithioethers ($RSCH_2CH_2SR$ or SS) toward the quadruply bonded $[Re_2X_8]^{2-}$ ion (X = Cl or Br) have yielded complexes of the type $Re_2X_5(SS)_2$, $Re_2X_6(SS)_2$ and $[Re_2Cl_7(SS)]^-$ with Re–Re triple and quadruple bonds [1–4]. However, no examples of $Re_2Cl_4(SS)_2$ compounds have been reported despite the fact that many $Re_2Cl_4(PP)_2$ compounds are known where PP is a diphosphine ligand [5]. In an effort to synthesize $Re_2Cl_4(dth)_2$ where dth = 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$), we have explored the reaction of dth with $Re_2Cl_4(PEt_2Ph)_4$ where Et = ethyl and Ph = phenyl. To our surprise, the product is the new Re_2^{7+} face-sharing bioctahedral complex $Re_2(\mu\text{-}SCH_3)_3Cl_4(PEt_2Ph)_2$ (**1**).

Since the yield for this reaction was quite low, we sought a better route to such Re_2^{7+} complexes. Organic disulfides (RSSR) and diselenides (RSeSeR) had previously been utilized to prepare Re_2^{6+} edge-sharing bioctahedral complexes such as $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ and $Re_2(\mu\text{-}SePh)_2Cl_4(dppm)_2$ where dto and dppm are the bidentate ligands 3,6-dithiaoctane and bis(diphenylphosphino)methane, respectively [6,7]. We now report that face-sharing bioctahedral complexes of the type $Re_2(\mu\text{-}SR)_3X_4L_2$ where X is Cl or Br and L is a monodentate phosphine ligand can be readily prepared in moderate yield by the reaction of organic disulfides with either $Re_2X_4L_4$ or $Re_2X_5L_3$ compounds.

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2. Experimental

2.1. Materials and measurements

The dirhenium compounds $(n\text{-}Bu_4N)_2Re_2Cl_8$, $(n\text{-}Bu_4N)_2Re_2Br_8$, $Re_2Cl_4(PEt_2Ph)_4$, $Re_2Br_4(PEt_2Ph)_4$, and $Re_2Cl_5(PMePh_2)_3$ where Et = ethyl, Me = methyl and Ph = phenyl were prepared according to the published procedures [8–10]. The reagent 2,5-dithiahexane (dth) was purchased from Pfaltz and Bauer, and used as received. The phosphines PEt_2Ph and $PMePh_2$, the disulfides PhSSPh and EtSSEt, and HPLC-grade solvents were used as received from Aldrich. All reactions were carried out in a positive-pressure nitrogen atmosphere, with air-free techniques employed prior to isolation of final products. All products were determined to be air- and moisture-stable.

Magnetic moments (μ_{eff}) of compounds **1**–**5** were determined at room temperature (23 ± 1 °C) on an Evans magnetic susceptibility balance. X-ray diffraction studies were performed at the Laboratory for Molecular Structure and Bonding at Texas A&M University. X-ray crystallographic data parameters are listed in Table 1. A slight disorder of one of the methyl thiolate groups was found in compound **1**. The positions and relative occupancies of atoms corresponding to this group (labeled S3, C23, S3′, and C23′) were refined. The final refined occupancy of the major orientation (S3, C23) was 0.81(2).

2.2. Synthesis of $Re_2(\mu\text{-}SMe)_3Cl_4(PEt_2Ph)_2$ (1)

$Re_2Cl_4(PEt_2Ph)_4$ (0.102 g, 0.0865 mmol) was combined with 2,5-dithiahexane (0.12 ml, 1.0 mmol) in 30 ml toluene. This solution was stirred and refluxed for 24 h. The resulting mixture consisted of a purple solution and a very small amount of dark purple solid. Additional product was obtained in crystalline form by layering hexane over the reaction solution and allowing slow diffusion to take place for 1 week. Yield: 0.0056 g (6.9%).

In a second preparation, $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.5716 g, 0.5010 mmol), PEt_2Ph (0.50 g, 3.0 mmol) and methyl disulfide (0.24 ml, 2.7 mmol) were mixed together in 50 ml of CH_2Cl_2 and 5 ml of toluene. This mixture was stirred and refluxed for 16 h. Two-thirds of the solvent was removed by vacuum distillation, and the resulting deep purple solution was placed in a refrigerator at 5 °C. Purple crystals formed after 3 days. Yield: 0.076 g (15%).

Table 1
Crystal data and data collection parameters for compounds **1**, **2**, **3** and **4**

	1	2	3	4
Formula	$Re_2Cl_4S_3P_2C_{23}H_{39}$	$Re_2Cl_4S_3P_2C_{38}H_{45}\cdot C_3H_6O$	$Re_2Cl_4S_3P_2C_{44}H_{41}$	$Re_2Br_4S_3P_2C_{26}H_{45}$
Color and habit	dark red plate	dark red block	dark red plate	very dark red plate
Crystal size, mm	0.35 × 0.25 × 0.10	0.10 × 0.07 × 0.05	0.29 × 0.20 × 0.09	0.30 × 0.25 × 0.04
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	10.916(5)	12.510(4)	15.564(1)	18.032(2)
b (Å)	16.397(2)	12.852(2)	17.668(6)	11.149(2)
c (Å)	17.975(9)	27.780(6)	16.105(1)	17.962(1)
α (°)	90	90	90	90
β (°)	91.69(2)	93.30(2)	100.98(1)	102.18(1)
γ (°)	90	90	90	90
V (Å^3)	3216(2)	4459(2)	4348(2)	3529.8(8)
Z	4	4	4	4
Temperature (K)	293(2)	213(2)	213(2)	293(2)
Instrument	Nonius CAD4	Nonius FAST	Nonius FAST	Nonius FAST
Radiation	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
Scan method	θ–2θ	ellipsoid mask-fitting	ellipsoid mask-fitting	ellipsoid mask-fitting
θ Range	2.15–22.56	2.13–22.64	2.31–22.64	2.31–22.47
Total no. data	4471	16 237	18 097	14 743
No. unique data	4210 ($R_{int} = 0.0688$)	5848 ($R_{int} = 0.0944$)	5713 ($R_{int} = 0.0563$)	4538 ($R_{int} = 0.0911$)
No. observed, $I > 2\sigma(I)$	2736	4509	5270	3966
No. parameters [a]	316	328	572	334
Max., min. transmission	0.998, 0.218	0.745, 0.524	0.586, 0.246	0.345, 0.097
Absorption correction	psi scans	psi scans	psi scans	multi-scan
R [b] (all data)	0.122	0.127	0.039	0.080
R_w [c] (all data)	0.178	0.210	0.090	0.202
R (obs. data)	0.066	0.089	0.035	0.071
R_w (obs. data)	0.146	0.176	0.086	0.190

[a] In each structure, all hydrogen atoms were included at idealized positions and the form of the refinement was full-matrix least squares on F^2.

[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

This compound was also synthesized by the reaction of $Re_2Cl_4(PEt_2Ph)_4$ with MeSSMe. $Re_2Cl_4(PEt_2Ph)_4$ (0.2513g, 0.213 mmol) was dissolved in 25 ml of acetone. Methyl disulfide (0.10 ml, 1.1 mmol) was added and the solution was refluxed with rapid stirring for 16 h. The resulting purple solution was evaporated to dryness. The residue was dissolved in 3 ml of acetone and the product was precipitated by the slow addition of 12 ml of hexane. Yield: 0.137g (65.1%). *Anal.* Calc. for $C_{23}H_{39}Cl_4P_2S_3Re_2$: C, 27.96; H, 3.98. Found: C, 28.35; H, 4.10%. Vis λ_{max} (nm) in CH_2Cl_2: 459, 530. $\mu_{eff} = 1.81$ BM.

2.3. Synthesis of $Re_2(\mu\text{-}SPh)_3Cl_4(PEt_2Ph)_2\cdot$acetone (**2**)

$Re_2Cl_4(PEt_2Ph)_4$ (0.3073 g, 0.2606 mmol) was combined with phenyl disulfide (PhSSPh) (0.1707 g, 0.7818 mmol) in 25 ml of acetone. This mixture was refluxed with rapid stirring for 16 h. The resulting red–brown solution was evaporated under a stream of nitrogen gas at room temperature. The residue was dissolved in a minimum of acetone (5 ml) and layered with a double portion of cold hexanes. The layered mixture was held at −10 °C overnight and small single crystals were deposited. The dark purple product was filtered off and washed with diethyl ether. Yield: 0.2133 g (66.4%). *Anal.* Calc. for $C_{41}H_{51}Cl_4OP_2S_3Re_2$ (i.e. $Re_2(\mu\text{-}SPh)_3Cl_4(PEt_2Ph)_2\cdot(CH_3)_2CO$): C, 39.96; H, 4.17. Found: C, 41.73; H, 4.22%. Vis λ_{max} (nm) in CH_2Cl_2: 452, 540. $\mu_{eff} = 1.80$ BM.

2.4. Synthesis of $Re_2(\mu\text{-}SPh)_3Cl_4(PMePh_2)_2$ (**3**)

A mixture of $Re_2Cl_5(PMePh_2)_3$ (0.2503 g, 0.2176 mmol) and PhSSPh (0.1184 g, 0.5423 mmol) was refluxed in 20 ml of 1,2-dichloroethane for 50 h. The resulting solution was placed in a freezer at −10 °C for 1 week. A dark purple precipitate was filtered off and washed with cold diethyl ether. Yield: 0.2335 g, (86.39%). *Anal.* Calc. for $C_{44}H_{41}Cl_4P_2S_3Re_2$: C, 42.55; H, 3.33. Found: C, 43.51; H, 3.41%. Vis λ_{max} (nm) in CH_2Cl_2: 418, 455, 544. $\mu_{eff} = 1.82$ BM.

2.5. Synthesis of Re_2 $(\mu\text{-}SEt)_3Br_4(PEt_2Ph)_2$ (**4**)

This was prepared in 67% yield by the same method used to synthesize compound **2**, except that $Re_2Br_4(PEt_2Ph)_4$ and ethyl disulfide (EtSSEt) were used instead of $Re_2Cl_4(PEt_2Ph)_4$ and phenyl disulfide. *Anal.* Calc. for $C_{26}H_{45}Br_4P_2S_3Re_2$: C, 25.86; H, 3.76. Found: C, 26.34; H, 3.95%. Vis λ_{max} (nm) in CH_2Cl_2: 428, 586. $\mu_{eff} = 1.85$ BM.

2.6. Synthesis of $Re_2(\mu\text{-}SPh)_3Br_4(PEt_2Ph)_2$ (**5**)

This was prepared in 72% yield by the same method used to make compound **2**, except that $Re_2Br_4(PEt_2Ph)_4$ was used instead of $Re_2Cl_4(PEt_2Ph)_4$. *Anal.* Calc. for $C_{38}H_{45}Br_4P_2S_3Re_2$: C, 33.76; H, 3.35. Found: C, 34.61; H, 3.80%. Vis λ_{max} (nm) in CH_2Cl_2: 480, 585. $\mu_{eff} = 1.84$ BM.

3. Results and discussion

3.1. Syntheses

Compounds **1**–**5** with the general formula $Re_2(\mu\text{-}SR)_3X_4L_2$ where X = halide and L = monodentate tertiary phosphine were prepared in good yield by reacting either $Re_2X_4L_4$ complexes (Re–Re bond order = 3) or $Re_2X_5L_3$ complexes (Re–Re bond order = 2.5) with an excess of organic disulfides. As three thiolate ligands are added, the $Re_2X_4L_4$ complexes lose two phosphine ligands and no halide ligands, and the dirhenium core changes from Re_2^{4+} to Re_2^{7+}. However, one phosphine ligand and one chloride ligand are lost when the starting material is $Re_2Cl_5(PMePh_2)_3$ and the core changes from Re_2^{5+} to Re_2^{7+}. The net result in both cases is a product with nine ligands (or an M_2Y_9 compound). As noted above, Re_2^{6+} compounds of the type $Re_2(\mu\text{-}ER)_2X_4(LL)_2$ where E = S or Se and LL = bidentate dithioether or diphosphine were previously prepared by reactions of dirhenium complexes with ethyl disulfide or phenyl diselenide [6,7]. In these earlier reactions, only two thiolate ligands were added, but no bidentate ligands were lost and M_2Y_{10} compounds were produced. Apparently the nature of the neutral ligands (monodentate vs. bidentate) controls the number of thiolate ligands in the product and thus the oxidation states of the metal atoms.

Compound **1** was also prepared in low yield by carbon–sulfur bond cleavage in the reaction of $Re_2Cl_4(PEt_2Ph)_4$ with 2,5-dithiahexane ($MeSCH_2CH_2SMe$). Previously, several edge-sharing bioctahedral dimolybdenum complexes with bridging thiolate ligands were synthesized by similar C–S bond cleavage reactions involving dithioethers and complexes with multiple Mo–Mo bonds [11,12]. Compound **1** was prepared in somewhat higher yield by the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with MeSSMe and PEt_2Ph. It is possible that $Re_2Cl_4(PEt_2Ph)_4$ is produced in an initial stage of this reaction, although it normally requires much more time to generate significant amounts of this triply bonded dirhenium compound from the quadruply bonded $[Re_2Cl_8]^{2-}$ ion [10].

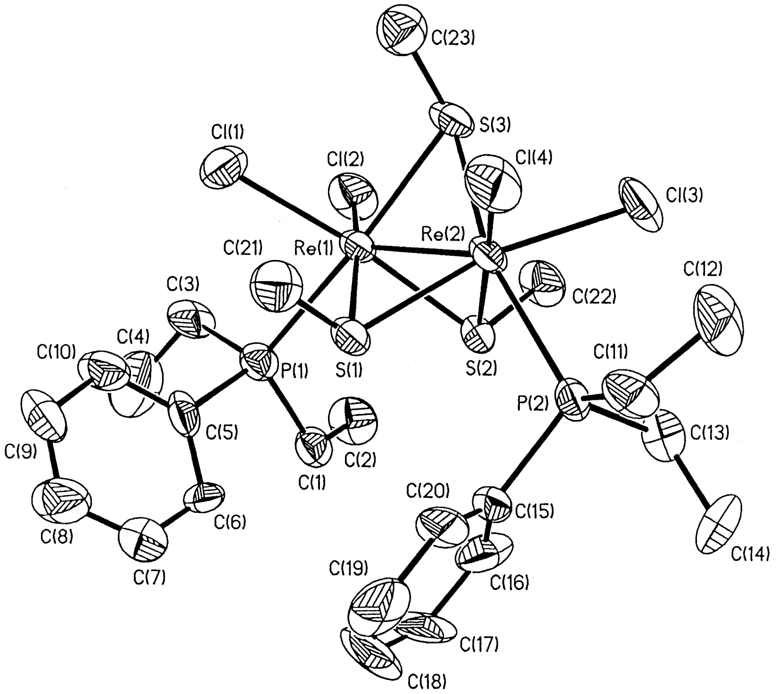

Fig. 1. Molecular structure of $Re_2(\mu\text{-}SMe)_3Cl_4(PEt_2Ph)_2$ (**1**). Hydrogen atoms are omitted for clarity.

3.2. Crystal structures

Figs. 1–4 illustrate the molecular structure of compounds **1**, **2**, **3**, and **4**, respectively. The coordination geometry about the dirhenium core in each molecule is best described as a face-sharing bioctahedron with C_{2v} symmetry. In each case, three thiolate ligands bridge two ReX_2PR_3 units with terminally bound halide (X) and phosphine (PR_3) ligands. The halides and phosphines are arranged such that each X–Re–Re–X and P–Re–Re–P moiety is essentially planar. Partial crystallographic analysis of a tiny crystal of compound **5** has

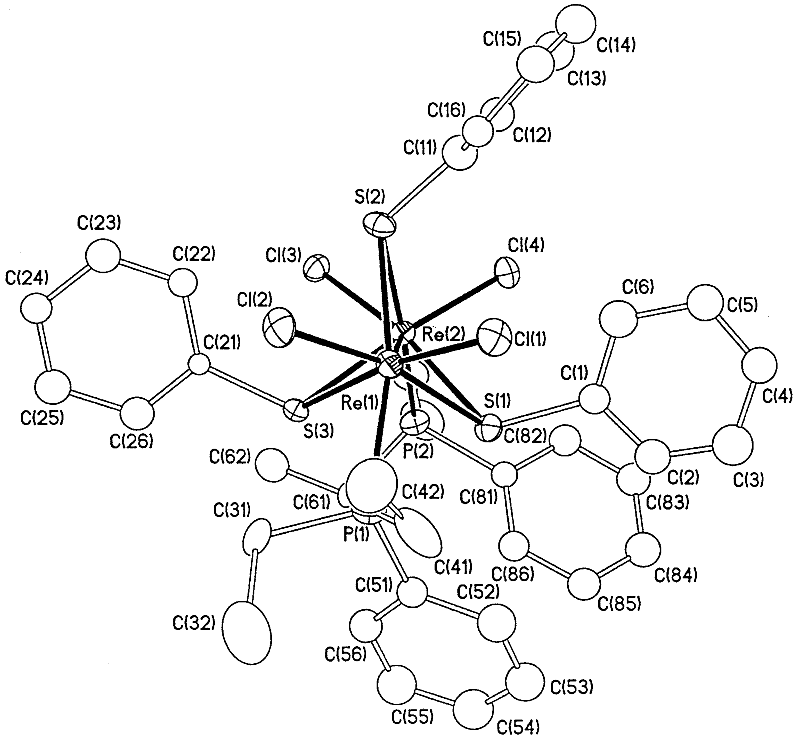

Fig. 2. Structure of the dirhenium molecule in $Re_2(\mu\text{-}SPh)_3Cl_4(PEt_2Ph)_2\cdot$acetone (**2**). Hydrogen atoms are omitted for clarity.

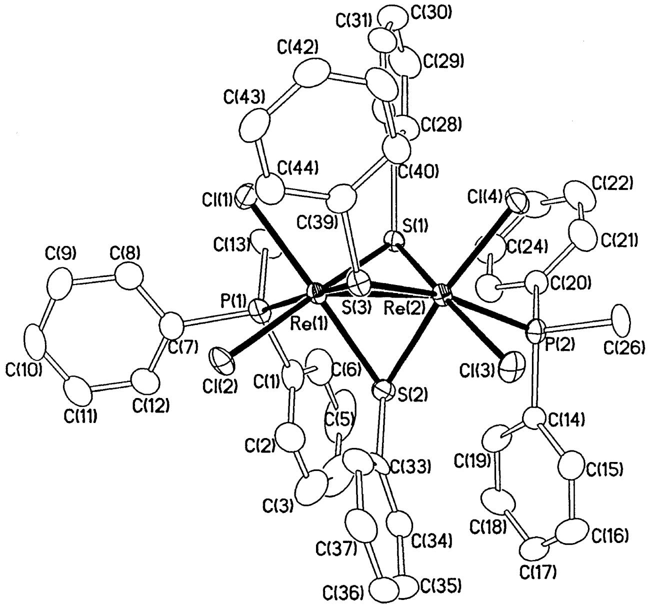

Fig. 3. Molecular structure of $Re_2(\mu\text{-}SPh)_3Cl_4(PMePh_2)_2$ (**3**). Hydrogen atoms are omitted for clarity.

yielded enough data to confirm that it has a similar structure [13]. Selected bond distances and angles for compounds **1**–**4** are listed in Tables 2–5. A summary of the core bond lengths and angles for all four compounds is presented in Table 6. The nature of the hydrocarbon portion of the thiolate ligands has little effect on the average Re–S bond distances and the average Re–S–Re angles since these remain essentially unchanged. In each of the three molecules containing chloride ligands, the Re–S bond lengths are longest for the sulfur atoms *trans* to the phosphine ligands. However, this is not the case in compound **4** where there are bromide instead of chloride ligands.

3.3. Magnetism and bonding

Room temperature magnetic susceptibility measurements reveal that compounds **1**–**5** are one-electron paramagnetic with $\mu_{\text{eff}} = 1.80–1.85$ BM. A simple MO approach to the bonding in face-sharing bioctahedral complexes (ignoring the complications of the bridging ligands) yields one sigma and two pi molecular orbitals available for metal–metal bonding [14]. An Re_2^{7+} system contributes seven electrons to these orbitals for a $\sigma^2\pi^4\pi^{*1}$ electronic configuration and an Re–Re bond order of 2.5. Such a bond order is consistent with the average Re–Re bond length of 2.473 Å in compounds **1**–**4** and the paramagnetism of these complexes.

4. Conclusion

Face-sharing bioctahedral complexes of the type $Re_2(\mu\text{-}SR)_3X_4L_2$ are produced when $Re_2X_4L_4$ or $Re_2X_5L_3$ compounds with monodentate ligands react with organic disulfides, in contrast to the edge-sharing bioctahedral complexes previously produced when $Re_2X_4(LL)_2$ compounds with bidentate ligands (LL)

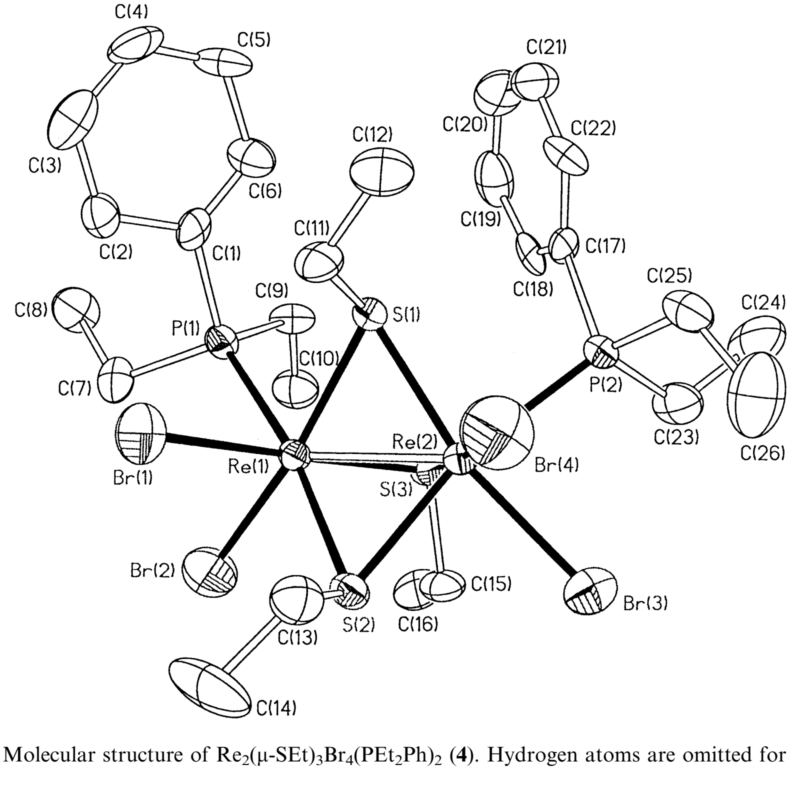

Fig. 4. Molecular structure of $Re_2(\mu\text{-}SEt)_3Br_4(PEt_2Ph)_2$ (**4**). Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for $Re_2(\mu\text{-}SMe)_3Cl_4(PEt_2Ph)_2$ (**1**)

Bond lengths	
Re(1)–Re(2)	2.458(2)
Re(1)–Cl(1)	2.366(6)
Re(1)–S(2)	2.375(5)
Re(1)–Cl(2)	2.376(6)
Re(1)–S(3)	2.393(8)
Re(1)–S(1)	2.350(6)
Re(1)–P(1)	2.524(6)
Re(2)–S(1)	2.357(6)
Re(2)–Cl(4)	2.361(7)
Re(2)–S(2)	2.388(6)
Re(2)–Cl(3)	2.397(7)
Re(2)–S(3)	2.401(8)
Re(2)–P(2)	2.531(6)
Bond angles	
S(1)–Re(1)–Cl(1)	94.5(2)
S(1)–Re(1)–S(2)	83.7(2)
Cl(1)–Re(1)–S(2)	174.3(2)
S(1)–Re(1)–Cl(2)	165.6(2)
Cl(1)–Re(1)–Cl(2)	89.2(2)
S(2)–Re(1)–Cl(2)	91.2(2)
S(1)–Re(1)–S(3)	109.8(2)
Cl(1)–Re(1)–S(1)	94.6(3)
S(2)–Re(1)–S(3)	91.0(3)
Cl(2)–Re(1)–S(3)	83.6(3)
S(1)–Re(1)–Re(2)	58.7(1)
Cl(1)–Re(1)–Re(2)	124.2(2)
S(2)–Re(1)–Re(2)	59.2(1)
Cl(2)–Re(1)–Re(2)	129.3(2)
S(3)–Re(1)–Re(2)	59.3(2)
S(1)–Re(1)–P(1)	82.2(2)
Cl(1)–Re(1)–P(1)	84.5(2)
S(2)–Re(1)–P(1)	90.0(2)
Cl(2)–Re(1)–P(1)	84.3(2)
S(3)–Re(1)–P(1)	168.0(2)
Re(2)–Re(1)–P(1)	130.6(2)
S(1)–Re(2)–Cl(4)	91.2(2)
S(1)–Re(2)–S(2)	83.3(2)
Cl(4)–Re(2)–S(2)	172.7(2)
S(1)–Re(2)–Cl(3)	167.7(2)
Cl(4)–Re(2)–Cl(3)	91.0(3)
S(2)–Re(2)–Cl(3)	93.3(2)
S(1)–Re(2)–S(3)	109.3(2)
Cl(4)–Re(2)–S(3)	95.8(3)
S(2)–Re(2)–S(3)	90.5(3)
Cl(3)–Re(2)–S(3)	82.5(3)
S(1)–Re(2)–Re(1)	58.4(1)
Cl(4)–Re(2)–Re(1)	122.1(2)
S(2)–Re(2)–Re(1)	58.7(1)
Cl(3)–Re(2)–Re(1)	129.3(2)
S(3)–Re(2)–Re(1)	59.0(2)
S(1)–Re(2)–P(2)	85.7(2)
Cl(4)–Re(2)–P(2)	89.6(2)
S(2)–Re(2)–P(2)	85.2(2)
Cl(3)–Re(2)–P(2)	82.3(2)
S(3)–Re(2)–P(2)	163.9(3)
Re(1)–Re(2)–P(2)	129.6(2)
Re(1)–S(1)–Re(2)	63.0(2)
Re(1)–S(2)–Re(2)	62.1(1)
Re(1)–S(3)–Re(2)	61.7(2)

Table 3
Selected bond distances (Å) and angles (°) for $Re_2(\mu\text{-}SPh)_3Cl_4(PEt_2Ph)_2 \cdot$ acetone (**2**)

Bond lengths	
Re(1)–Re(2)	2.474(2)
Re(1)–Cl(1)	2.358(6)
Re(1)–S(2)	2.432(6)
Re(1)–Cl(2)	2.376(6)
Re(1)–S(3)	2.387(6)
Re(1)–S(1)	2.374(6)
Re(1)–P(1)	2.534(7)
Re(2)–S(1)	2.374(6)
Re(2)–Cl(4)	2.351(6)
Re(2)–S(2)	2.424(6)
Re(2)–Cl(3)	2.399(6)
Re(2)–S(3)	2.385(6)
Re(2)–P(2)	2.525(6)
Bond angles	
Cl(1)–Re(1)–S(1)	91.0(2)
Cl(1)–Re(1)–Cl(2)	89.5(2)
S(1)–Re(1)–Cl(2)	167.1(2)
Cl(1)–Re(1)–S(2)	96.1(2)
S(1)–Re(1)–S(2)	106.5(2)
Cl(2)–Re(1)–S(2)	86.2(2)
Cl(1)–Re(1)–S(3)	171.2(2)
S(1)–Re(1)–S(3)	86.0(2)
Cl(2)–Re(1)–S(3)	91.5(2)
S(2)–Re(1)–S(3)	92.7(2)
Cl(1)–Re(1)–Re(2)	126.1(2)
S(1)–Re(1)–Re(2)	58.6(2)
Cl(2)–Re(1)–Re(2)	130.0(2)
S(2)–Re(1)–Re(2)	59.2(2)
S(3)–Re(1)–Re(2)	58.7(2)
Cl(1)–Re(1)–P(1)	87.7(2)
S(1)–Re(1)–P(1)	85.5(2)
Cl(2)–Re(1)–P(1)	81.6(2)
S(2)–Re(1)–P(1)	167.2(2)
S(3)–Re(1)–P(1)	83.8(2)
Re(2)–Re(1)–P(1)	127.3(2)
Cl(4)–Re(2)–S(1)	93.0(2)
Cl(4)–Re(2)–S(2)	95.3(2)
S(1)–Re(2)–S(2)	106.8(2)
Cl(4)–Re(2)–Cl(3)	90.0(2)
S(1)–Re(2)–Cl(3)	165.5(2)
S(2)–Re(2)–Cl(3)	86.9(2)
Cl(4)–Re(2)–S(3)	171.6(2)
S(1)–Re(2)–S(3)	86.0(2)
S(2)–Re(2)–S(3)	92.9(2)
Cl(3)–Re(2)–S(3)	88.9(2)
Cl(4)–Re(2)–Re(1)	127.4(2)
S(1)–Re(2)–Re(1)	58.6(1)
S(2)–Re(2)–Re(1)	59.5(2)
Cl(3)–Re(2)–Re(1)	128.8(2)
S(3)–Re(2)–Re(1)	58.8(2)
Cl(4)–Re(2)–P(2)	82.7(2)
S(1)–Re(2)–P(2)	82.5(2)
S(2)–Re(2)–P(2)	170.5(2)
Cl(3)–Re(2)–P(2)	83.8(2)
S(3)–Re(2)–P(2)	88.9(2)
Re(1)–Re(2)–P(2)	128.7(1)
Re(1)–S(1)–Re(2)	62.8(2)
Re(1)–S(2)–Re(2)	61.3(2)
Re(1)–S(3)–Re(2)	62.5(2)

Table 4
Selected bond distances (Å) and angles (°) for $Re_2(\mu\text{-}SPh)_3Cl_4(PMePh_2)_2$ (**3**)

Bond lengths	
Re(1)–Re(2)	2.4870(8)
Re(1)–S(1)	2.374(2)
Re(1)–Cl(2)	2.378(2)
Re(1)–S(2)	2.388(2)
Re(1)–S(3)	2.413(2)
Re(1)–Cl(1)	2.366(2)
Re(1)–P(1)	2.553(2)
Re(2)–Cl(4)	2.366(2)
Re(2)–S(1)	2.373(2)
Re(2)–S(2)	2.389(2)
Re(2)–Cl(3)	2.396(2)
Re(2)–S(3)	2.428(2)
Re(2)–P(2)	2.545(2)
Bond angles	
Cl(1)–Re(1)–S(1)	92.79(6)
Cl(1)–Re(1)–Cl(2)	89.79(7)
S(1)–Re(1)–Cl(2)	163.15(6)
Cl(1)–Re(1)–S(2)	173.97(7)
S(1)–Re(1)–S(2)	84.57(6)
Cl(2)–Re(1)–S(2)	91.19(7)
Cl(1)–Re(1)–S(3)	93.49(6)
S(1)–Re(1)–S(3)	107.61(6)
Cl(2)–Re(1)–S(3)	88.83(7)
S(2)–Re(1)–S(3)	92.48(6)
Cl(1)–Re(1)–Re(2)	124.24(5)
S(1)–Re(1)–Re(2)	58.38(5)
Cl(2)–Re(1)–Re(2)	131.91(5)
S(2)–Re(1)–Re(2)	58.65(4)
S(3)–Re(1)–Re(2)	59.38(4)
Cl(1)–Re(1)–P(1)	84.89(6)
S(1)–Re(1)–P(1)	81.60(7)
Cl(2)–Re(1)–P(1)	82.06(7)
S(2)–Re(1)–P(1)	89.35(6)
S(3)–Re(1)–P(1)	170.74(6)
Re(2)–Re(1)–P(1)	128.69(5)
Cl(4)–Re(2)–S(1)	91.37(6)
Cl(4)–Re(2)–S(2)	168.01(7)
S(1)–Re(2)–S(2)	84.57(6)
Cl(4)–Re(2)–Cl(3)	89.90(7)
S(1)–Re(2)–Cl(3)	167.25(6)
S(2)–Re(2)–Cl(3)	91.63(7)
Cl(4)–Re(2)–S(3)	99.90(6)
S(1)–Re(2)–S(3)	107.17(6)
S(2)–Re(2)–S(3)	92.08(6)
Cl(3)–Re(2)–S(3)	85.09(6)
Cl(4)–Re(2)–Re(1)	128.00(5)
S(1)–Re(2)–Re(1)	58.43(4)
S(2)–Re(2)–Re(1)	58.59(5)
Cl(3)–Re(2)–Re(1)	129.04(5)
S(3)–Re(2)–Re(1)	58.80(4)
Cl(4)–Re(2)–P(2)	83.82(6)
S(1)–Re(2)–P(2)	87.35(6)
S(2)–Re(2)–P(2)	84.73(6)
Cl(3)–Re(2)–P(2)	80.17(6)
S(3)–Re(2)–P(2)	164.81(6)
Re(1)–Re(2)–P(2)	129.70(4)
Re(1)–S(1)–Re(2)	63.20(5)
Re(1)–S(2)–Re(2)	62.75(5)
Re(1)–S(3)–Re(2)	61.82(5)

Table 5
Selected bond distances (Å) and angles (°) for $Re_2(\mu\text{-}SEt)_3Br_4(PEt_2Ph)_2$ (**4**)

Bond lengths	
Re(1)–Re(2)	2.4734(9)
Re(1)–S(1)	2.355(4)
Re(1)–S(2)	2.388(4)
Re(1)–S(3)	2.411(4)
Re(1)–Br(1)	2.489(2)
Re(1)–Br(2)	2.512(2)
Re(1)–P(1)	2.531(4)
Re(2)–S(1)	2.361(4)
Re(2)–S(2)	2.380(4)
Re(2)–S(3)	2.397(4)
Re(2)–Br(4)	2.460(3)
Re(2)–P(2)	2.531(5)
Re(2)–Br(3)	2.541(2)
Bond angles	
S(1)–Re(1)–S(2)	108.7(2)
S(1)–Re(1)–S(3)	85.32(14)
S(2)–Re(1)–S(3)	89.05(14)
S(1)–Re(1)–Re(2)	58.48(10)
S(2)–Re(1)–Re(2)	58.60(10)
S(3)–Re(1)–Re(2)	58.77(11)
S(1)–Re(1)–Br(1)	94.22(11)
S(2)–Re(1)–Br(1)	92.28(12)
S(3)–Re(1)–Br(1)	178.67(11)
Re(2)–Re(1)–Br(1)	122.01(6)
S(1)–Re(1)–Br(2)	165.85(12)
S(2)–Re(1)–Br(2)	84.97(12)
S(3)–Re(1)–Br(2)	91.45(12)
Re(2)–Re(1)–Br(2)	130.51(7)
Br(1)–Re(1)–Br(2)	88.69(8)
S(1)–Re(1)–P(1)	81.16(14)
S(2)–Re(1)–P(1)	170.04(14)
S(3)–Re(1)–P(1)	93.25(14)
Re(2)–Re(1)–P(1)	130.45(10)
Br(1)–Re(1)–P(1)	85.44(11)
Br(2)–Re(1)–P(1)	85.29(12)
S(1)–Re(2)–S(2)	108.8(2)
S(1)–Re(2)–S(3)	85.50(14)
S(2)–Re(2)–S(3)	89.56(14)
S(1)–Re(2)–Br(4)	91.38(13)
S(2)–Re(2)–Br(4)	92.80(13)
S(3)–Re(2)–Br(4)	176.57(12)
S(1)–Re(2)–Re(1)	58.25(10)
S(2)–Re(2)–Re(1)	58.91(10)
S(3)–Re(2)–Re(1)	59.31(10)
Br(4)–Re(2)–Re(1)	120.05(8)
S(1)–Re(2)–P(2)	84.1(2)
S(2)–Re(2)–P(2)	166.7(2)
S(3)–Re(2)–P(2)	88.1(2)
Br(4)–Re(2)–P(2)	90.13(14)
Re(1)–Re(2)–P(2)	129.66(11)
S(1)–Re(2)–Br(3)	167.26(12)
S(2)–Re(2)–Br(3)	83.86(12)
S(3)–Re(2)–Br(3)	93.06(12)
Br(4)–Re(2)–Br(3)	89.66(10)
Re(1)–Re(2)–Br(3)	131.13(7)
P(2)–Re(2)–Br(3)	83.23(13)
Re(1)–S(1)–Re(2)	63.27(11)
Re(2)–S(2)–Re(1)	62.49(11)
Re(2)–S(3)–Re(1)	61.92(10)

Table 6
Comparison of core structural features of $Re_2(\mu\text{-}SR)_3X_4L_2$ compounds **1**–**4**

Distance (Å) or angle (°)	R = Me, X = Cl L = PEt_2Ph (**1**)	R = Ph, X = Cl L = PEt_2Ph (**2**)	R = Ph, X = Cl L = $PMePh_2$ (**3**)	R = Et, X = Br L = PEt_2Ph (**4**)
Re–Re	2.458(2)	2.474(2)	2.4870(8)	2.4734(9)
Shortest Re–S	2.350(6)	2.374(6)	2.373(2)	2.355(4)
Longest Re–S	2.401(8)	2.424(6)	2.428(2)	2.411(4)
Avg. Re–S	2.38(1)	2.40(2)	2.39(2)	2.38(2)
Avg. Re–P	2.528(6)	2.530(6)	2.549(2)	2.536(4)
Avg. Re–S–Re	62.3(4)	62.2(5)	62.6(2)	62.6(5)
Avg. Re–Re–P	130.1(2)	128.0(6)	129.2(1)	130.1(2)

were reacted with RSSR. A significant amount of multiple metal–metal bonding is retained in these new air-stable, paramagnetic Re_2^{7+} complexes. It is now our intention to determine the types of complexes that result from the reactions of disulfides with compounds of the type $Re_2X_6L_2$ and $Re_2X_5(LL)_2$.

5. Supplementary material

Crystallographic data are available on request from the 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), quoting CCDC numbers 196200 (**1**), 196201 (**2**), 196202 (**3**) and 196203 (4).

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