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Substitution reactivity of the hydrido sulfido bridged dirhenium complex $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_8]$ (naph = 2-naphthyl)

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The substitution reactivity of the hydrido sulfido bridged dirhenium complex $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_8]$ **1** (naph = 2-naphthyl) has been investigated. The former complex can be easily substituted with one equivalent of tmno (trimethylamine-*N*-oxide) followed by addition of a ligand L giving complexes of the general formula $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7L]$ [L = NCMe (**2a**), NC(Bu^t) (**2b**), pyridine (**2c**), PH_3 (**2d**), PMe_3 (**2e**), $H_2P(p\text{-}C_6H_4OMe)$ (**2f**), PPh_3 (**2g**), $P(OMe)_3$ (**2h**)]. L is always perpendicularly co-ordinated to one of the Re atoms with respect to the Re–(μ-SR)–Re plane. In case of ligands with small cone angles two isomers are found. They differ in the relative orientation of L with respect to the substituent R attached to the sulfido bridge (*syn* and *anti* isomer). Temperature dependent 2D-EXSY NMR experiments with **2a** dissolved in $CDCl_3$ proved that both isomers are in a dynamic equilibrium, which is based on the pyramidal inversion of the bridging sulfur. The thermodynamic data of this process at 298.15 K were determined to be: $\Delta G^{\ddagger} = 68.6 \pm 1.2$ kJ mol^{-1}, $\Delta H^{\ddagger} = 49.0 \pm 4.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -66 \pm 21$ J K^{-1} mol^{-1}. Owing to intramolecular sterical hindrance ligands with large cone angles give only the *anti* isomer. Disubstituted complexes $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_6L_2]$ [L = NCMe (**3a**), pyridine (**3b**), PPh_3 (**3c**)] and $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_6(\mu\text{-}L\text{–}L)]$ [L–L = dppm (**4a**), dppe (**4b**)] were prepared in a similar way. The reaction of $[Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8]$ **5** with one equivalent of tmno and PPh_3 gave $[Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_6(PPh_3)_2]$ **6** in 38% yield. Compound **6** is rigid on the timescale of ^{31}P NMR spectroscopy. The molecular structures of **2a**, **2c**, **2g**, **2h**, **3a**, **4b** and **6** were confirmed by X-ray structure analyses.

Introduction

The chemistry of polynuclear sulfido bridged (μ-SR) metal complexes is very rich.[1] Almost every transition metal forms such complexes with one, two or three sulfido ligands bridging a metal–metal vector. The sulfido bridge has to be considered as a three-electron donor ligand having one lone pair of electrons left. In many of these complexes the sulfido bridges are non-rigid ligands due to pyramidal inversion of the bridging sulfur atom. The low inversion energy is a consequence of metal–sulfur interaction. The metal reduces the s-character of the lone pair ground state allowing easier access to the transition state in which the inverting lone pair of electrons is regarded as having pure p-character. In addition, pπ–dπ overlap of sulfur and metal orbitals reduces the energy barrier for pyramidal inversion as well giving in many cases configurationally non-rigid molecules.[2] Typical values for the sulfur atomic inversion energy $\Delta G^{\ddagger}$ in sulfido bridged complexes range from 45 to 80 kJ mol^{-1}.[2,3] There are many reports on the chemistry of dinuclear sulfido bridged complexes of manganese and rhenium,[4] but only few refer to such stereodynamic processes. For example, in the case of the complexes $[M_2(\mu\text{-}SR)_2(CO)_8]$ (M = Mn, Re; R = H, organic residue), only for R = H is the inversion of the bridging sulfur mentioned.[5] The similar molecules $[M_2(\mu\text{-}PR_2)(\mu\text{-}SR')(CO)_8]$ (M = Mn, Re; R, R′ = organic residue)[6] and $[Re_2(\mu\text{-}ER)(\mu\text{-}E'R')(CO)_8]$ (E, E′ = S, Se, Te; R, R′ = organic residue)[7] are known to show evidence of pyramidal inversion at room temperature. Rate constants and thermodynamic data were not determined in any of these cases.

We have recently reported the synthesis the sulfido bridged complexes $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ (R = H, organic residue)[8] and now wish to report on the facile synthesis and characterisation of their substitution products. The investigations focused on $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_8]$ **1** (naph = 2-naphthyl) as the 2-naphthyl residue facilitates crystallisation of the prepared compounds. Starting from **1**, the mono- and di-substituted products $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7L]$ and $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_6L_2]$ (L = two-electron donor ligand) were prepared and the different substitution patterns with respect to the cone angle of L were explored. In addition the observed pyramidal inversion of the bridging sulfur in $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7NCMe]$ **2a** was examined by 2D-EXSY NMR spectroscopy.[9]

Results and discussion

Monosubstituted complexes $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7L]$ (naph = 2-naphthyl)

On treating $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_8]$ **1** with one equivalent of tmno (trimethylamine-*N*-oxide) at 0 °C in THF, one CO ligand is removed. Subsequent addition of one equivalent of a ligand L generates the complexes $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7L]$ **2** [L = NCMe (**2a**), NC(Bu^t) (**2b**), pyridine (**2c**), PH_3 (**2d**), PMe_3 (**2e**), $H_2P(p\text{-}C_6H_4OMe)$ (**2f**), PPh_3 (**2g**), $P(OMe)_3$ (**2h**)] in good yields (Scheme 1). Compound **2d** was obtained from the reaction of **1** with $P(SiMe_3)_3$ and subsequent methanolysis. Naturally, their *ν*(CO) spectra (not shown) are very similar, showing seven absorptions and suggesting that all complexes have an analogous structure. On the basis of the X-ray structure analyses of **2a**, **2c**, **2g** and **2h** we conclude that L is always axially bound [perpendicular with respect to the Re–(μ-SR)–Re plane]. The chemical shift of the μ-H ligand in these complexes is strongly dependent on the ligand L. In general, on substitution a low field shift of the μ-H resonance relative to **1** is observed.

Complexes substituted by ligands with small cone angles according to Tolman[10] (**2a**, **2b**, **2d**, **2f**) consist of two isomers as evidenced by two high field shifted ^{1}H NMR signals of the μ-H ligands. These signals must be attributed to a *syn* and an *anti*

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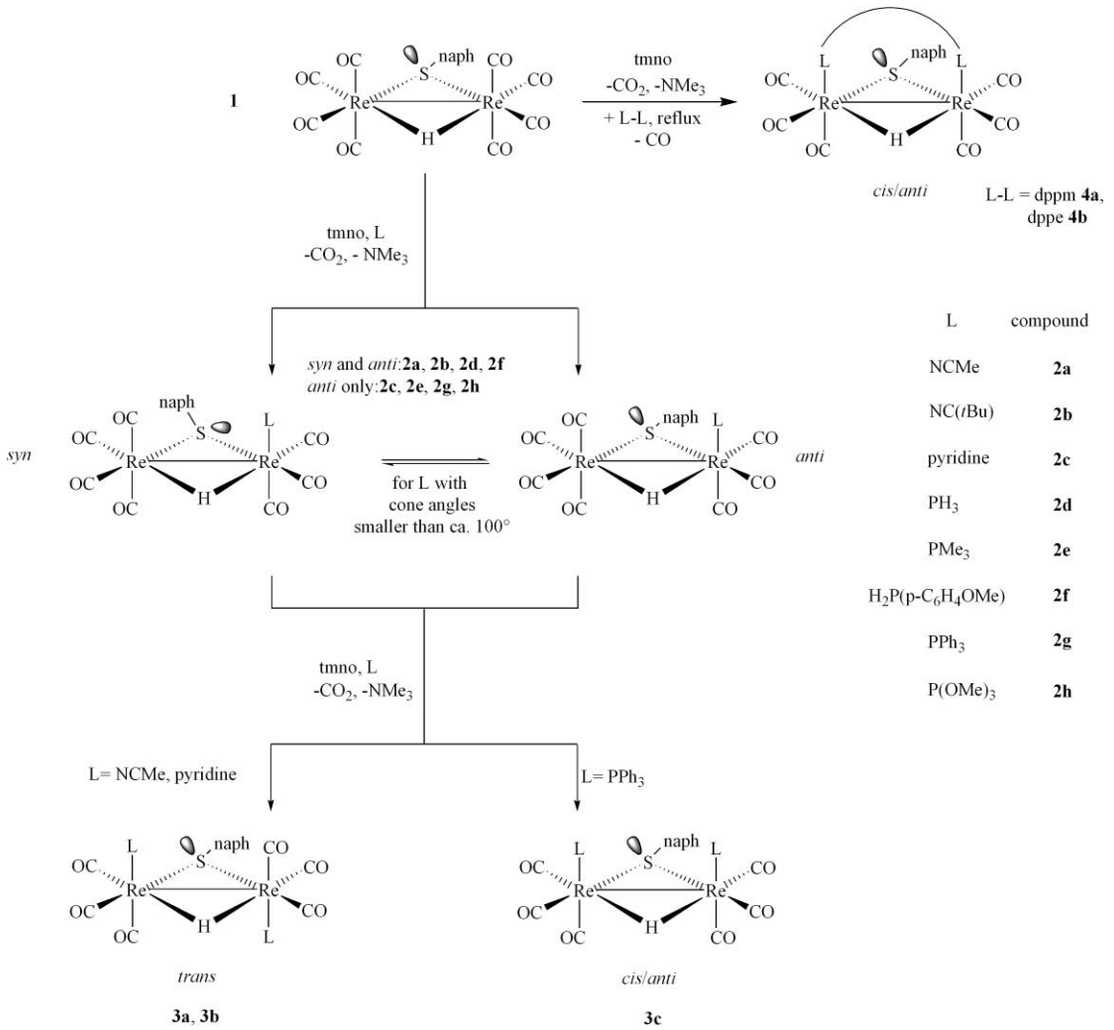


Scheme 1 Preparation of substitution products of **1**.

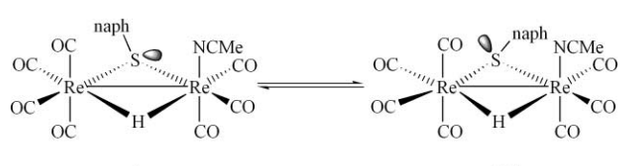
isomer. The isomers differ in the relative orientation of L with respect to the 2-naphthyl residue attached to the bridging sulfur atom. The ratio strongly depends on the solvent used. We have investigated this dependence for **2a** as this is the only pair of isomers allowing assignment of *syn* and *anti* isomer by ^{1}H NMR spectroscopy. The *syn* isomer always exhibits the resonance of the methyl group of the acetonitrile ligand at high field (1.21 ppm in $CDCl_3$) whereas the corresponding resonance of the *anti* isomer is located at lower field (2.33 ppm in $CDCl_3$). The assignment of *syn* or *anti* is based on a comparison with other acetonitrile complexes of rhenium[11] like, for example, $[Re_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)(CO)_7(NCMe)]$ [δ(Me) = 2.20 in CD_2Cl_2].[11b] In all of these cases the signal of the methyl group of acetonitrile is located well above 2 ppm. The unusual high field shift of one of the methyl groups in the **2a** experiments is most likely caused by an electronic shielding effect of the neighbouring 2-naphthyl residue. Therefore we assign this signal to the *syn* isomer, and consequently the signal at δ = 2.33 to the *anti* isomer. The *syn* : *anti* ratios of **2a** in various solvents are summarised in Table 1. The ratio of isomers was determined by integration of the signals of the μ-H ligands or of the methyl resonances of the acetonitrile ligands, respectively. Apparently, the sterically favoured *anti* isomer predominates in all solvents but dichloromethane and chloroform. From chloroform–hexane, *syn*-**2a** crystallised as confirmed by a single crystal X-ray analysis.

Table 1 *syn* : *anti* Ratio of **2a** in various solvents according to ^{1}H NMR data

syn : *anti*	Solvent	Polarity of solvent
1 : 1.37	CD_3CN	0.65
1 : 1.22	d_6-Acetone	0.56
1 : 1.12	d_8-THF	0.45
1 : 0.68	CD_2Cl_2	0.42
1 : 0.67	$CDCl_3$	0.40
1 : 1.07	d_6-Benzene	0.32

Interconversion of *syn* and *anti* isomers

The above-described results indicated that *syn* and *anti* isomers are interconverting. In order to verify this hypothesis, variable-temperature ^{1}H NMR spectra of **2a** in $CDCl_3$ were recorded. Upon heating, the signals of the μ-H ligands coalescenced at 310 K confirming a fluxional process. On further heating to 320 K the H^1 signals of the 2-naphthyl group coalescenced, and finally upon heating to 330 K only one sharp resonance for the μ-H ligands and for the H^1 protons remained. At this point the signals of the acetonitrile ligand are very broad, but coalescence of their resonances was not yet reached. Since no free acetonitrile was observed the detected dynamic process is almost certainly based on the inversion of the sulfido bridge (Scheme 2). In **2a** the inversion of the sulfido bridge proceeds



Scheme 2 Interconversion of *syn* and *anti* isomers of **2a**.

even at 298.4 K, as established by a ^{1}H 2D-EXSY[9] NMR spectrum recorded in $CDCl_3$. From that spectrum the rate constant of the interconversion was determined to be 6.03 ± 0.05 s^{-1}. Its value was calculated from the integrals of the acetonitrile resonances according to literature procedures.[9] Further 2D-EXSY spectra were recorded at 308.0, 314.9 and 322.3 K. At 322.3 K, however, the solution turned yellow within 3 hours indicating slow decomposition of **2a**. From the remaining data, Eyring activation parameters at 298.15 K were calculated by plotting $\ln(k/T)$ *vs.* $1/T$ giving $\Delta G^{\ddagger}$ = 68.6 ± 1.2 kJ mol^{-1}, $\Delta H^{\ddagger}$ = 49.0 ± 4.2 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −66 ± 21 J K^{-1} mol^{-1}. As these data are based on three temperatures only, their margin of error is quite big. Nevertheless $\Delta S^{\ddagger}$ is negative, strongly suggesting an intramolecular rearrangement by pyramidal inversion of the sulfido bridge. Moreover, the value of $\Delta G^{\ddagger}$ is close to those derived for other sulfido bridged transition metal complexes like $[HOs_3(\mu\text{-SMe})(\mu_3\text{-}\eta^2\text{-}C_6H_4)(CO)_9]$ ($\Delta G^{\ddagger}$ = 61.5 kJ mol^{-1})[3d] or $[Mo_2(CO)_3(\mu\text{-SR})_3(\eta^7\text{-}C_7H_7)]$ [$\Delta G^{\ddagger}$ = 61.9, 58.8 kJ mol^{-1} (for R = Me, Bu^t)].[3e] In order to find out whether the residue attached to the bridging sulfur has a significant influence on the inversion process the 2-naphthyl residue in **2a** was replaced by the stronger electron withdrawing C_6F_5 residue. It became immediately apparent that the inversion barrier is lowered in this case. A ^{1}H NMR spectrum of $[Re_2(\mu\text{-H})(\mu\text{-}SC_6F_5)(CO)_7NCMe]$ **2i** in $CDCl_3$ recorded at 300 K shows only one μ-H resonance and two broad resonances for the methyl groups of the acetonitrile ligand. Hence, the signals of the μ-H ligands have already coalescenced due to faster inversion of the sulfido bridge at this temperature. The C_6F_5 group is probably stabilising the planar transition state by p(sulfur)⟶ $\pi^*(C_6F_5)$ orbital overlap.[2] From the big variety of monosubstituted complexes prepared we can conclude that those substituted by ligands L with cone angles larger than approximately 100° (**2c**, **2e**, **2g**, **2h**) exhibit only the *anti* isomer as confirmed by a single ^{1}H NMR resonance for the μ-H ligand. A hypothetical *syn* isomer is unlikely to exist in these cases due to steric repulsion between the 2-naphthyl residue and the bulky ligand L. A comparison of these results with other hydrido sulfido bridged metal complexes would be most desirable. However, for most of these complexes there is no indication whether they are dynamic with respect to pyramidal inversion of sulfur or not. For example, the analogous manganese complexes $[Mn_2(\mu\text{-H})(\mu\text{-SR})(CO)_8]$ are known to be stable compounds, but so far only three examples have been obtained in very low yield preventing a closer inspection of their chemical properties.[12] The inversion of sulfur has been characterised for the complexes $[Ir_2(\mu\text{-H})(\mu\text{-SR})Cp^*_2Cl_2]$ as being not rapid on the NMR timescale,[13] but this statement is too vague for comparison with the above-described complex. Since complexes like $[Re_2(\mu\text{-SPh})(ER)(CO)_8]$ (E = S, Se, Te)[7] and $[Re_2(\mu\text{-PCy}_2)(\mu\text{-SPh})(CO)_8]$ [6a] also exhibit pyramidal inversion of sulfur at room temperature, we conclude that the inversion in systems with a $Re_2(\mu\text{-Y})(\mu\text{-SR})$ (Y = bridging ligand) core is not strongly dependent upon the bridging ligand Y.

Disubstituted complexes $[Re_2(\mu\text{-H})(\mu\text{-Snaph})(CO)_6L_2]$ and $[Re_2(\mu\text{-H})(\mu\text{-Snaph})(CO)_6(\mu\text{-L–L})]$

Disubstituted derivatives of **1** were prepared starting from the monosubstituted precursors **2a**, **2c**, **2g**. The latter were reacted with one equivalent of tmno and subsequently one equivalent of ligand L giving the disubstituted complexes $[Re_2(\mu\text{-H})(\mu\text{-Snaph})(CO)_6L_2]$ [L = NCMe (**3a**), pyridine (**3b**), PPh_3 (**3c**)] in 70–75% yield. In **3a** and **3b** each rhenium is axially substituted by one of the ligands L which are arranged *trans* to each other (Scheme 1) as established by ^{1}H NMR spectra. We have no indication that the sulfido bridge in these complexes is fluxional as in **2a**. ^{1}H NMR spectra of **3a** in $CDCl_3$ at 45 °C show a slight broadening of the methyl resonances. At higher temperatures the complex slowly decomposes, most likely due to dissociation of the labile NCMe. In **3c** the PPh_3 ligands are co-ordinated *cis* to each other and *anti* with respect to the 2-naphthyl residue due to their bulkiness. The two different types of substitution pattern can be distinguished by ν(CO) IR spectroscopy. The *trans* substituted products exhibit three absorption bands, whereas in **3c** an analogous pattern with an additional band at 1952 cm^{-1} is observed.

The substitution of **1** by bidentate ligands like dppe [1,2-bis(diphenylphoshino)ethane] or dppm [bis(diphenylphospino)methane] is best performed by reacting a THF solution of it with one equivalent of tmno and subsequent addition of one equivalent of these ligands followed by heating to reflux for several hours. The expected substitution products $[Re_2(\mu\text{-H})(\mu\text{-Snaph})(CO)_6(\mu\text{-L–L})]$ [L–L = dppm (**4a**), dppe (**4b**)] were obtained in 90% yield. Reacting **1** with two equivalents of tmno at 0 °C in THF and subsequent addition of dppm or dppe, respectively, gives the same products, but the yields are distinctly lower (about 30%). In both products the bidentate ligands are bridging the two rhenium atoms. As expected they are co-ordinated in an *anti* orientation with respect to the 2-naphthyl residue. The structure of **4b** has been confirmed by a single crystal X-ray analysis.

All attempts to prepare triply substituted derivatives of **1** by tmno substitution, heating or irradiation in the presence of an excess of ligand failed, giving disubstituted products only and confirming the high thermodynamic stability of the $Re(CO)_3$ units that has been observed for other sulfido bridged rhenium carbonyl complexes.[14]

Substitution of $[Re_2(\mu\text{-H})(\mu\text{-SH})(CO)_8]$ 5 with PPh_3

The substitution of CO ligands in $[Re_2(\mu\text{-H})(\mu\text{-SH})(CO)_8]$ **5** was tested with tmno and PPh_3. Although only one equivalent of the latter compound was used $[Re_2(\mu\text{-H})(\mu\text{-SH})(CO)_6(PPh_3)_2]$ **6** was the main product (40% yield). The reaction was accompanied by strong decomposition reactions. According to ^{1}H NMR and ^{31}P NMR spectra **6** was contaminated with small amounts of an unknown phosphorus-containing compound [^{31}P($CDCl_3$): δ = 43.9] which was lost on recrystallisation from chloroform–hexane. A single crystal X-ray analysis revealed that in **6** the two PPh_3 ligands are co-ordinated in a *trans* arrangement confirming that the *cis* arrangement in **3c** is based on steric factors only. The ^{1}H NMR spectrum exhibits triplets for the μ-H ligand (δ = −12.88, J_{PH} = 7.7 Hz) and for the hydrogen attached to the sulfido bridge (δ = −1.08, J_{PH} = 10.0 Hz) due to coupling with the PPh_3 ligands. The strong highfield shift of the latter hydrogen resonance is typical for SH bridged molecules {*e.g.* $[Re_2(\mu\text{-SH})_2(CO)_8]$ δ(H) = −0.89;[15] **6** δ(μ-SH) = −0.47}.[8] The ^{31}P NMR spectrum shows two sharp resonances at δ = 11.3 and 15.8 proving that the molecule is rigid on the timescale of ^{31}P NMR spectroscopy, since on rapid inversion of the sulfido bridge only one resonance would have been expected.

Molecular structures of 2a, 2c, 2g, 3a, 4b and 6

These compounds exhibit equal molecular structures with almost planar $Re_2(\mu\text{-H})(\mu\text{-S})$ cores. The basic structural elements of this type of molecular structure have been discussed earlier.[8] So the following will focus on the most interesting differences only.

Compound **2a** (see Fig. 1) differs from the already reported molecular structure of $[Re_2(\mu\text{-H})(\mu\text{-Snaph})(CO)_8]$ **1**[8] in the substitution of an axially co-ordinated CO group with an acetonitrile ligand which is in the sterically less favoured *syn* position to the 2-naphthyl group. The crystallisation of this isomer is in agreement with the above discussed dynamics since the crystal was grown from a solution of **2a** in chloroform in which the *syn* isomer predominates. Unfortunately all attempts to crystallise the *anti* isomer from acetone or acetonitrile, respectively, in which the *anti* isomer predominates failed as no

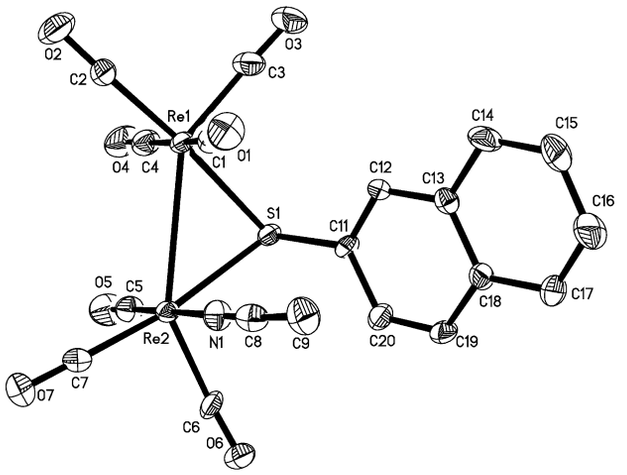


Fig. 1 Molecular structure of **2a**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1023(12), Re1–S1 2.480(2), Re2–S1 2.478(2), Re2–N1 2.150(8), S1–C11 1.788(9); S1–Re1–Re2 51.24(6), S1–Re2–Re1 51.29(5), Re1–S1–Re2 77.47(7).

single crystals were obtained. The Re–Re single bond is slightly elongated to 3.1023(12) Å [3.0909(8) Å in the unsubstituted complex] but the two equal Re–S distances remain unchanged. A rather large torsion angle of 9.5(4)° is observed for C1–Re1–Re2–N1 and the acetonitrile ligand bends towards the 2-naphthyl group [S1–Re2–N 87.4(2)°] whereas the carbonyl group 1 bends away from it [S1–Re1–C1 97.3(3)°]. This is obviously due to the steric interactions of these ligands with the 2-naphthyl group. The 2-naphthyl group is twisted around the S1–C11 axis, the angle between the plane of C11–C20 and the Re–Re vector is 17.1(1)° and the Re1–S1–C11–C12 and Re1–S1–C11–C20 torsion angles are 32.9(9) and 65.5(8)°, respectively (absolute values).

The μ-H position was not determined from Fourier maps, but the orientation of the equatorial CO groups 2 and 7 with Re–Re–C angles of 124.8(3) and 120.0(3)°, respectively, as well as Orpen's HYDEX program [16] strongly indicate a position in the Re_2S plane midway between the carbonyl ligands. This is in agreement with the crystallographically determined μ-H positions in $Re_2(\mu\text{-H})(\mu\text{-SPh})(CO)_8$ [8] and **4b** and **6**.

Complex **2c** (see Fig. 2) exhibits two crystallographically independent but geometrically almost identical molecules per asymmetric unit. The structure differs from **2a** in the substitution of one axial CO group by a pyridine ligand instead of acetonitrile, but now the ligand is positioned *anti* to the 2-naphthyl group. In view of the fact that in solution only one isomer is present we conclude that the latter is the *anti* isomer too. Compared with **2a** the Re–Re and Re–S bond parameters remain unaffected. Concerning the μ-H position the same considerations are valid as for **2a**.

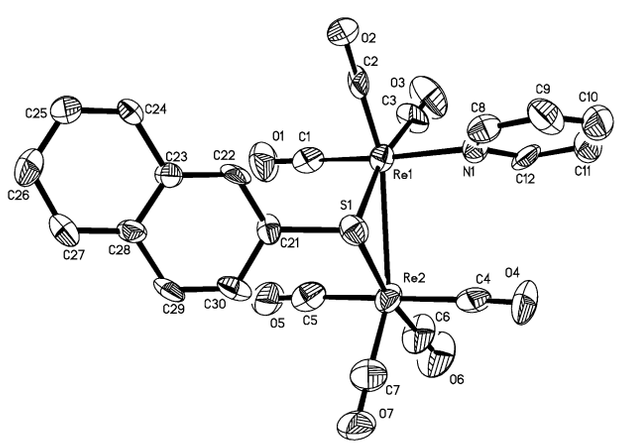


Fig. 2 Molecular structure of **2c**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): molecule 1: Re1–Re2 3.1093(15), Re1–N1 2.27(2), Re1–S1 2.477(7), Re2–S1 2.465(6), S1–C21 1.77(2); S1–Re1–Re2 50.83(13), S1–Re2–Re1 51.18(15), Re1–S1–Re2 77.99(18); molecule 2: Re3–Re4 3.1054(15), Re3–S2 2.482(6), Re4–N2 2.225(17), Re4–S2 2.469(7), S2–C51 1.80(2); S2–Re3–Re4 50.97(17), S2–Re4–Re3 51.34(15), Re3–S2–Re4 77.69(18).

In **2g** (see Fig. 3) the substituting ligand is triphenylphosphine, again in a position *anti* to the 2-naphthyl group. A hypothetical *syn* co-ordination is impossible as the van der Waals radii of PPh_3 and the 2-naphthyl residue would overlap. Hence, in solution only the *anti* isomer is present. The Re–Re bond is clearly elongated to 3.1238(13) Å but the Re–S distances are the same as for **2a** and **2c**. The μ-H position is deduced the same way as above.

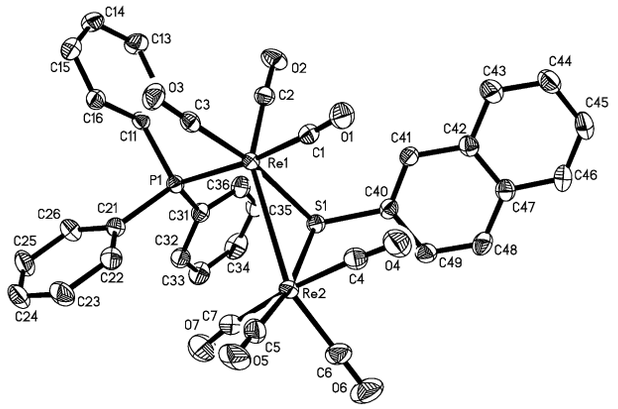


Fig. 3 Molecular structure of **2g**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1238(13), Re1–P1 2.488(2), Re1–S1 2.479(2), Re2–S1 2.465(2), S1–C40 1.790(5); P1–Re1–Re2 97.93(5), S1–Re1–Re2 50.60(4), S1–Re2–Re1 51.03(4), Re1–S1–Re2 78.37(5).

Compound **3a** (see Fig. 4) is a twofold substituted complex with acetonitrile ligands co-ordinated at both Re atoms. These ligands are in the sterically favourable *trans* position to each other, thus the one attached to Re1 is *anti* to the 2-naphthyl group and the one attached to Re2 is in the *syn* position. This constitution is in full agreement with the assignment from the spectroscopic solution data. As observed for **2a** the molecule exhibits a large C3–Re1–Re2–N2 torsion angle of 9.2(6)° and

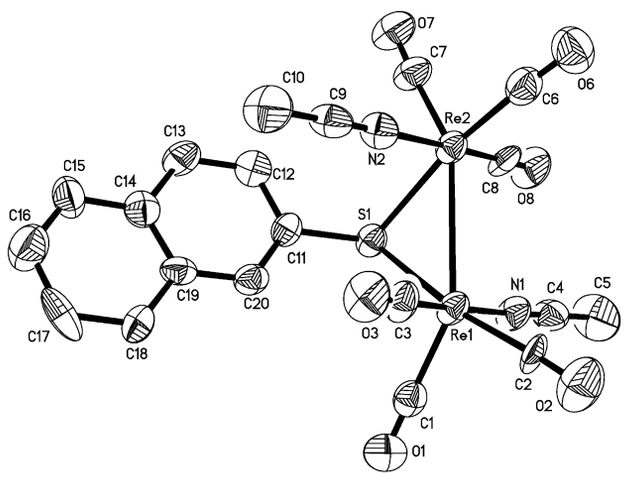


Fig. 4 Molecular structure of **3a**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1049(11), Re1–N1 2.138(13), Re1–S1 2.485(4), Re2–N2 2.136(14), Re2–S1 2.486(4), S1–C11 1.780(16); N1–Re1–S1 85.4(4), N1–Re1–Re2 84.7(4), S1–Re1–Re2 51.36(10), N2–Re2–S1 85.9(4), N2–Re2–Re1 86.1(4), S1–Re2–Re1 51.34(9), Re1–S1–Re2 77.30(12).

bending of the CO(3) and acetonitrile N(2) ligands [S1–Re1–C3 98.8(5)°, S1–Re2–N2 85.9(4)°], accompanied by the twist of the 2-naphthyl group along the S1–C11 axis with torsion angles of Re1–S–C11–C20 36.7(15)° and Re2–S–C11–C12 62.9(13)°, respectively (absolute values). The other pair of axial ligands, CO(8) and acetonitrile N(1) show an undistorted eclipsed arrangement along the Re–Re vector with N1–Re1–Re2–C8 of 0.1(6)°. The Re–Re bond length of 3.1049(11) Å and the μ-H position is the same as for **2a** and **2c**.

A 1,2-bis(diphenylphosphino)ethane group (dppe) serves as the bridging ligand in **4b** (see Fig. 5). Each Re atom is attached

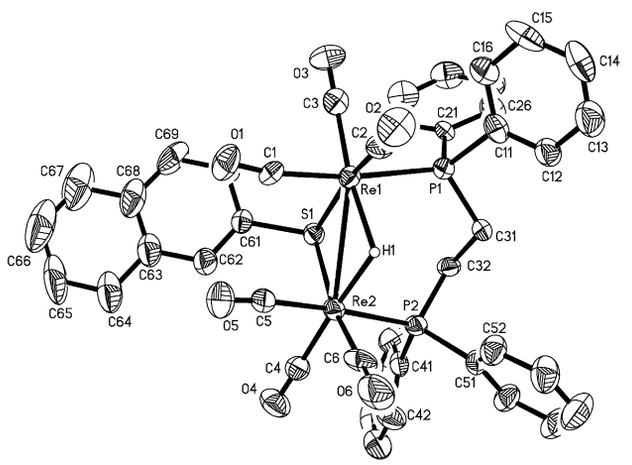


Fig. 5 Molecular structure of **4b**. Hydrogen atoms omitted except μ-H. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1427(7), Re1–P1 2.477(2), Re1–S1 2.505(2), Re2–P2 2.464(2), Re2–S1 2.490(2), S1–C61 1.811(9), C31–C32 1.509(12); P1–Re1–S1 93.72(7), P1–Re1–Re2 99.80(6), S1–Re1–Re2 50.81(5), P2–Re2–S1 85.79(8), P2–Re2–Re1 97.78(6), S1–Re2–Re1 51.22(5), Re1–S1–Re2 77.97(7).

to one P atom in axial position and the dppe ligand is *anti* to the 2-naphthyl group. A hypothetical *syn* isomer cannot exist owing to the same reason pointed out for **2g**. Consequently, in solution only the *anti* isomer is present. The corresponding Re_2S and Re_2P_2 planes show a dihedral angle of 97.6(1)°. The dppe chelate ligand leads to a prominent enlargement of the Re–Re single bond to 3.1427(7) Å and the Re–S distances tend to be slightly elongated compared with those of the preceding compounds. The steric strain caused by dppe results also in torsion angles of the carbonyl and the phosphine ligands along the Re–Re vector from 5.7(5) to 8.7(5)° (absolute values). The μ-H atom was derived from a Fourier map in the expected position.

Compound **6** (see Fig. 6) is a disubstituted complex with a PPh_3 ligand attached to each of the Re atoms. These two ligands show the sterically favourable *trans* arrangement for their axial positions confirming the assignment based on spectroscopic solution data. The distortion of the eclipsed ligand arrangement is only small with C–Re–Re–C and P–Re–Re–C torsion angles in the range from 0.2(2) to 4.9(2)° (absolute values). Re–S distances are similar to those of **2a**–**3a** but the Re–Re bond length of 3.1783(4) Å is unexpectedly the largest of this series of compounds. The μ-H atom was located from a Fourier map but the position of the μ-S bonded hydrogen atom could not be determined.

Experimental

General conditions

All reactions were performed in oxygen-free solvents which were dried according to literature methods, distilled and stored under an argon atmosphere. TLC was carried out on glass plates (20 × 20 cm) coated with a mixture of gypsum and silica gel (Merck 60 PF_{254}; 1 mm thick).

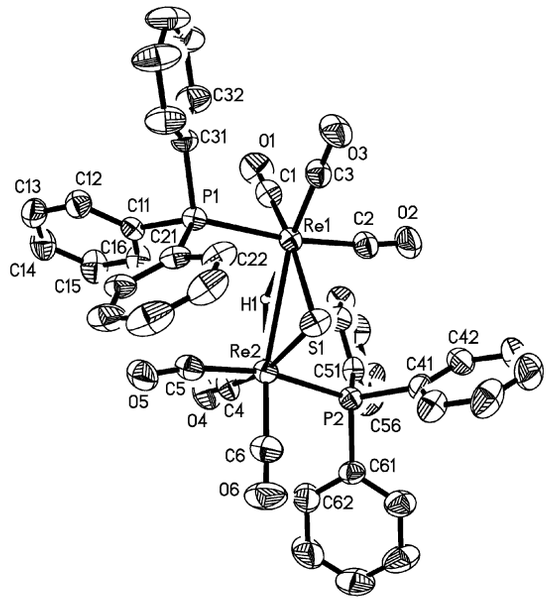


Fig. 6 Molecular structure of **6**. Hydrogen atoms omitted except μ-H. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1783(4), Re1–S1 2.4891(16), Re1–P1 2.4946(14), Re2–S1 2.4929(16), Re2–P2 2.4897(15); S1–Re1–P1 94.48(5), S1–Re1–Re2 50.41(4), P1–Re1–Re2 93.87(3), S1–Re2–P2 97.42(5), P2–Re2–Re1 100.63(4), S1–Re2–Re1 50.31(4), Re1–S1–Re2 79.28(4).

Instrumentation

The reaction products were characterised by ν(CO) FTIR spectroscopy (Nicolet P510; CaF_2 optics); ^1H and ^{31}P NMR spectroscopy (Bruker AMX 300).

2D EXSY NMR spectra of 2a

The experiments were performed and analysed according to the pulse sequence given in the literature.[9a] The mixing time τ_m was 150 ms and the temperatures were determined by an internal methanol thermometer (accuracy ±0.1 °C). The rate constants of the *syn* : *anti* interconversion were determined from the cross-peak to diagonal-peak intensity ratio of the methyl groups of the MeCN ligands at δ = 1.21 and 2.33.

Starting materials

The compounds tmno·$2H_2O$, PPh_3, dppm, dppe and $P(OMe)_3$ were received from Fluka. PMe_3 was purchased from Strem. $H_2P(p\text{-}C_6H_4OMe)$,[17] $P(SiMe_3)_3$[18] and $Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8$ (R = 2-naphthyl, C_6F_5 and H)[8] were prepared according to literature procedures. The tmno used in the reactions described below was liberated from water by sublimation.

Preparations

Monosubstituted complexes $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_7L]$ [R = 2-naphthyl, L = NCMe (2a), $NC(Bu^t)$ (2b), pyridine (2c), PH_3 (2d), PMe_3 (2e), $H_2P(p\text{-}C_6H_4OMe)$ (2f), PPh_3 (2g), $P(OMe)_3$ (2h); R = C_6F_5, L = NCMe (2i)]. 200 mg (0.264 mmol) of **1** were dissolved in 10 ml THF and cooled to 0 °C. Subsequently 20 mg (0.266 mmol) of tmno were added. The solution turned pale yellow and was stirred for 30 min, thereupon the solvent was removed. To the pale yellow residue was added one equivalent of ligand L and the resulting mixture was redissolved in dichloromethane. After 1 h of stirring the solution was taken to dryness and the residue subjected to TLC (eluent dichloromethane–hexane = 1 : 1 except for L = PPh_3: 1 : 5). In all cases two fractions were obtained. The one with the higher R_f-value contained small amounts (<5%) of educt **1**. The second fraction was pure $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7L]$ **2**. For the preparation

of **2d** the ligand $P(SiMe_3)_3$ was used. In this case the resulting dichloromethane solution was stirred for 1 h as described above, but then 10 ml of methanol were added and the reaction mixture was stirred for another 18 h. During this period the co-ordinated ligand was hydrolysed to give co-ordinated PH_3. The final working up sequence was performed as described above. The synthesis of **2i** is completely analogous to the synthesis of **2a**. Elemental analysis (yield): **2a** (50%) Found: C, 29.42; H, 1.42; N, 1.61. $C_{19}H_{11}O_7NRe_2S$ requires: C, 29.65; H, 1.44; N 1.82%. **2b** (68%) Found: C, 32.36; H, 1.98; N, 1.50. $C_{22}H_{17}O_7NRe_2S$ requires: C, 32.55; H, 2.11; N, 1.73%. **2c** (77%) Found: C, 32.88; H, 1.87; N, 1.44. $C_{22}H_{13}O_7NRe_2S$ requires: C, 32.71; H, 1.62; N, 1.73%. **2d** (38%) Found: C, 26.77; H, 1.45. $C_{17}H_{11}O_7PRe_2S$ requires: C, 26.77; H, 1.44%. **2e** (51%) Found: C, 30.27; H, 2.07. $C_{20}H_{17}O_7PRe_2S$ requires: C, 29.85; H, 2.13%. **2f** (65%) Found: C, 32.45; H, 1.63. $C_{23}H_{15}O_7PRe_2S$ requires: C, 32.93; H, 1.80%. **2g** (78%) Found: C, 42.20; H, 2.27. $C_{35}H_{23}O_7PRe_2S$ requires: C, 42.42; H, 2.34%. **2h** (65%) Found: C, 28.36; H, 2.16. $C_{20}H_{17}O_{10}PRe_2S$ requires: C, 28.17; 2.01%. **2i** (39%) Found: C, 21.90; H, 0.41; N, 1.65. $C_{15}H_4F_5NO_7Re_2S$ requires: C, 22.25; H, 0.50; N, 1.73%. Spectroscopic data (^{a} = ^{e} = signal of major isomer, ^{b} = ^{f} = signal of minor isomer): ν(CO) IR/cm^{-1} (THF): **2a** 2102 m, 2029 vs, 2006 s, 1950 m, 1925 s. **2b** 2102 m, 2030 vs, 2006 s, 1954 m, 1927 s. **2c** 2102 m, 2023 vs, 2006 s, 1991 m, 1952 m, 1917 s. **2d** 2102 m, 2033 vs, 2009 s, 1927 s. **2e** 2102 m, 2023 vs, 2006 vs, 1991 s, 1948 m, 1915 s, 1907 m. **2f** 2102 m, 2023 vs, 2008 s, 1944 m, 1913 s. **2g** 2102 m, 2027 vs, 2004 s, 1992 m, 1952 m, 1938 m, 1923 s. **2h** 2104 m, 2035 vs, 2006 s, 1995 sh, 1950 m, 1925 m, 1902 s. **2i** 2106 m, 2035 vs, 2010 s, 1996 s, 1961 m, 1940 m, 1928 m. ^{1}H NMR ($CDCl_3$): **2a** δ −11.95 (s, μ-H$_{syn}$), −11.90 (s, μ-H$_{anti}$), 1.21 (s, Me$_{syn}$), 2.33 (s, Me$_{anti}$), 7.50–7.43 (m, naph), 7.80–7.70 (m, naph), 7.92 (s, H$^1_{syn}$, naph), 8.05 (s, H$^1_{anti}$, naph). **2b** δ −11.88 (s, μ-H)^a, −11.87 (s, μ-H)^b, 0.64 (s, Bu^t)^a, 1.40 (s, Bu^t)^b, 7.38–7.49 (m, naph), 7.51–7.83 (m, naph), 7.95 [s, H^1(naph)]^a, 8.07 [s, H^1(naph)]^b. **2c** δ −10.77 (s, 1H, μ-H), 7.27–7.32 (m, 2H, py), 7.43–7.54 (m, 2H, naph), 7.76–7.85 (m, 5H, naph, py), 8.15 [s, 1H, H^1(naph)], 8.78 (d, $^3J_{HH}$ = 5.2 Hz, 2H, py). **2d** δ −13.83 (d, $^2J_{PH}$ = 8.3, μ-H)^a, −13.70 (d, $^2J_{PH}$ = 8.6 Hz, μ-H)^b, 3.34 (d, $^1J_{PH}$ = 349 Hz, PH_3)^b, 3.99 (d, $^1J_{PH}$ = 348 Hz, PH_3)^a, 7.29–8.03 (m, naph). **2e** δ −13.35 (d, $^2J_{PH}$ = 9.2 Hz, 1H, μ-H), 1.68 (d, $^2J_{PH}$ = 8.8 Hz), 7.46–7.58 (m, 2H, naph), 7.60–7.93 (m, 4H, naph), 8.13 [s, 1H, H^1 (naph)]. **2f** δ −13.64 (d, $^2J_{PH}$ = 8.6 Hz, μ-H)^e, −13.54 (d, $^2J_{PH}$ = 9.1 Hz, μ-H)^f, 3.97 (dd, $^1J_{PH}$ = 350 Hz, $^2J_{HH}$ = 6.4 Hz, PH)^b, 4.22 (dd, $^1J_{PH}$ = 350 Hz, $^2J_{HH}$ = 6.2 Hz, PH)^b, 3.79 (s, OMe)^a, 3.86 (s, OMe)^b, 6.78–8.06 (m, 11H, naph, Ph). **2g** δ −12.91 (d, $^2J_{PH}$ = 8.6 Hz, 1H, μ-H), 7.44–7.83 (m, 21H, naph, Ph), 8.09 [s, 1H, H^1 (naph)]. **2h** δ −13.75 (d, $^2J_{PH}$ = 12.1 Hz, 1H, μ-H), 3.73 (d, $^3J_{PH}$ = 11.4 Hz, 9H, Me), 7.41–7.53 (m, 2H, naph), 7.71–7.82 (m, 4H, naph), 8.05 [s, 1H, H^1(naph)]. **2i** δ −11.88 (s, μ-H), 2.05 (s, broad, Me), 2.37 (s, broad, Me). ^{31}P NMR ($CDCl_3$): **2d** δ −160.4 (q, $^1J_{PH}$ = 349 Hz, PH_3)^a, −159.7 (q, $^1J_{PH}$ = 347 Hz, PH_3)^b. **2e** δ −40.9 (s, PMe_3). **2f** δ −73.2 [t, $^1J_{PH}$ = 351 Hz, H_2P-(*p*-C_6HOMe)]^a, −71.6 [t, $^1J_{PH}$ = 350 Hz, H_2P(*p*-C_6HOMe)]^b. **2g** δ 10.9 (s, PPh_3). **2h** δ 118.9 [s, $P(OMe)_3$].

Disubstituted complexes $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_6L_2]$ [L = NCMe (3a), pyridine (3b), PPh_3 (3c)]. The preparation was started with 200 mg of the monosubstituted complexes $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_7L]$ [L = NCMe (0.269 mmol), pyridine (0.248 mmol), PPh_3 (0.202 mmol)]. The complexes were reacted with one equivalent of tmno as described above for the monosubstituted complexes. Addition of another equivalent of ligand L and TLC [eluent dichloromethane–hexane = 1 : 1 (**3a**, **3b**), 1 : 2 (**3c**)] gave pure $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_6L_2]$. Elemental analysis (yield): **3a** (73%) Found: C, 30.99; H, 1.80. $C_{20}H_{14}O_6N_2Re_2S$ requires: C, 30.69; H, 1.80%. **3b** (70%) Found: C, 35.99; 2.03. $C_{26}H_{18}O_6Re_2S$ requires: C, 36.36; H, 2.11%. **3c** (75%) Found: C, 50.71; H, 2.54. $C_{52}H_{38}O_6P_2Re_2S$ requires: C, 50.97; H, 3.13%. ν(CO) IR/cm^{-1} (THF): **3a** 2031 m, 2013 vs, 1917 vs. **3b** 2027 m, 2010 vs, 1915 vs. **3c** 2033 m, 2011 s, 1952 m, 1911 vs. ^{1}H NMR ($CDCl_3$): **3a** δ −10.15 (s, 1H, μ-H), 1.14 (s, 3H, Me$_{syn}$), 2.30 (s, 3H, Me$_{anti}$), 7.38–7.80 (m, 6H, naph), 8.06 [s, 1H, H^1(naph)]. **3b** δ −7.70 (s, 1H, μ-H), 6.89 [s(broad), 4H, py], 7.29–7.96 (m, 9H, naph, py), 8.46 [s(broad), 4H, py]. **3c** δ 11.70 (t, $^2J_{PH}$ = 8.5 Hz, 1H, μ-H), 7.22–7.85 (m, 36H, Ph, naph), 7.95 [s, 1H, H^1(naph)]. ^{31}P NMR ($CDCl_3$): **3c** δ 8.3 (s, PPh_3).

Disubstituted complexes $[Re_2(\mu\text{-}H)(\mu\text{-}Snaph)(CO)_6(\mu\text{-}L\text{–}L)]$ [L–L = dppm (4a), dppe (4b)]. 200 mg (0.264 mmol) of **1** were reacted with one equivalent of tmno in THF at 0 °C as described above. Now one equivalent of L–L was added and the mixture was refluxed for 8 h. Removal of the solvent and TLC (eluent dichloromethane–hexane = 1 : 1) gave pure **4a** and **4b**. Elemental analysis (yield): **4a** (90%) Found: C, 45.18; H, 2.47. $C_{41}H_{30}O_6P_2Re_2S$ requires: C, 45.38; H, 2.79%. **4b** (95%) Found: C, 45.76; H, 2.62. $C_{42}H_{32}O_6P_2Re_2S$ requires: C, 45.90; H, 2.93%. ν(CO) IR/cm^{-1} (THF): **4a** 2038 vs, 2013 s, 1952 m, 1932 m, 1915 s. **4b** 2037 vs, 2013 s, 1952 m, 1929 m, 1915 s. ^{1}H NMR ($CDCl_3$): **4a** δ −12.53 (t, $^2J_{PH}$ = 9.6 Hz, 1H, μ-H), 2.65 (m, 1H, CH_2), 3.42 (m, 1H, CH_2), 7.26–7.87 (m, 26H, Ph, naph), 8.20 [s, 1H, H^1(naph)]. **4b** δ −12.62 (t, $^2J_{PH}$ = 10.5 Hz, 1H, μ-H), 2.28 [s(broad), 2H, CH_2], 2.53 [s(broad), 2H, CH_2]; 7.39–7.95 (m, 26H, Ph, naph), 8.28 [s, 1H, H^1(naph)]. ^{31}P NMR ($CDCl_3$): **4a** δ 2.6 (s, dppm). **4b** δ −1.64 (s, dppe).

Substitution of $Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8$ 5 with PPh_3

A mixture of 25 mg (0.095 mmol) of PPh_3 and 60 mg (0.095 mmol) of **5** was dissolved at 0 °C in 10 ml of THF. Upon addition of one equivalent of tmno the colour of the solution turned pale yellow. After 20 min the colour turned to brown indicating decomposition reactions. The reaction was brought to an end after 1 h of stirring at room temperature by removing the solvent. The brown residue was worked up by TLC (eluent dichloromethane–hexane = 1 : 2) giving one fraction that contained $Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_6(PPh_3)_2$ **6** and an organic phosphorus compound. The latter was removed by recrystallisation from $CHCl_3$–*n*-pentane affording pure **6**. Elemental analysis (yield): (38%) Found: C, 45.53; H, 2.65. $C_{42}H_{32}O_6P_2SRe_2$ requires: C, 45.90; H, 2.93%. ν(CO) IR/cm^{-1} (THF): 2100 w, 2015 vs, 1934 s, 1917 s. ^{1}H NMR ($CDCl_3$): δ 12.88 (t, $^2J_{PH}$ = 7.7 Hz, 1H, μ-H), −1.05 (t, $^3J_{PH}$ = 9.9 Hz, 1H, SH), 7.45–7.58 (m, 30H, Ph). ^{31}P NMR ($CDCl_3$): δ 11.3 (s, PPh_3), 15.8 (s, PPh_3).

Crystal structure determinations

Pertinent crystallographic data for compounds **2a**, **2c**, **2g**, **3a**, **4b** and **6** are summarised in Table 2. All data sets were collected on a Bruker AXS P4 diffractometer with graphite monochromated Mo-Kα radiation. Standard reflections monitored after every 400 reflections showed only random deviations for **2a**, **2c**, **2g**. For **3a** a decrease of 16% was monitored, for **4b** 6% and for **6** 7%. The intensities of these three data sets were corrected accordingly. Intensities of all data sets were corrected for Lorentz-polarisation effects and absorption corrections *via* ψ-scans were applied. The structures were solved by direct and conventional Fourier methods. Full-matrix, least-squares structure refinement based on F^2. All apart from hydrogen atoms were refined anisotropically; geometrically placed hydrogen atoms were refined with a 'riding model' and $U(H) = 1.2U(C_{iso})$. The μ-H atom positions of structures **4b** and **6** were determined from ΔF maps. The μ-H atoms for **2a**, **2c**, **2g**, **3a** and the H atom attached to μ-S in **6** were not located and not included in the refinement. Programs used for calculations: SHELX-97.[19]

CCDC reference numbers 169418 **2a**, 139434 **2c**, 169419 **2g**, 169420 **3a**, 169421 **4b**, and 169422 **6**.

See http://www.rsc.org/suppdata/dt/b1/b107859c/ for crystallographic data in CIF or other electronic format.

Table 2 Crystallographic data

Compound	**2a**	**2c**	**2g**	**3a**	**4b**	**6**
Formula	$C_{19}H_{11}NO_7Re_2S$	$C_{22}H_{13}NO_7Re_2S$	$C_{35}H_{23}O_7PRe_2S$·toluene	$C_{20}H_{14}N_2O_6Re_2S$	$C_{42}H_{32}O_6P_2Re_2S$·acetone	$C_{42}H_{32}O_6P_2Re_2S$
M	769.7	806.8	1083.1	782.8	1157.2	1099.1
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$Pca2_1$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
T/K	208(2)	298(2)	208(2)	298(2)	293(2)	293(2)
a/Å	9.845(4)	15.464(5)	11.030(6)	13.619(3)	16.715(4)	10.615(1)
b/Å	13.269(4)	15.262(4)	12.673(6)	13.340(3)	18.225(3)	10.683(1)
c/Å	16.632(6)	20.333(3)	15.972(6)	14.345(2)	15.022(3)	19.747(2)
α/°			76.24(2)			75.86(1)
β/°	102.11(2)		71.27(2)	116.48(2)	108.41(1)	78.98(1)
γ/°			67.31(2)			68.87(1)
U/Å^3	2124.3(13)	4799(2)	1934(2)	2332.7(8)	4342.0(15)	2012.3(3)
Z	4	8	2	4	4	2
μ(Mo-Kα)/mm^{-1}	11.52	10.21	6.39	10.49	5.74	6.19
Reflections measured/unique	4796/4657	6828/5936	8955/8652	6189/5144	11 764/9962	10 631/9164
R_1[a]/wR_2[b]	0.043/0.115	0.061/0.127	0.035/0.093	0.071/0.194	0.056/0.111	0.036/0.084

[a] $R_1[F > 4\sigma(F)] = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2(F^2, \text{all data}) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

References

1 Recent examples: F. Takagi, H. Seino, Y. Mizobe and M. Hidai, *Can. J. Chem.*, 2001, **79**, 632; A. R. Dias, M. H. Garcia, M. J. Villa de Brito and A. Galvao, *J. Organomet. Chem.*, 2001, **632**, 75; Y. Nishibayashi, I. Wakiji, K. Hirata, M. Rakowski DuBois and M. Hidai, *Inorg. Chem.*, 2001, **40**, 578; S. M. T. Abedin, K. A. Azam, M. B. Hursthouse, S. E. Kabir, K. M. A. Malik, M. A. Mottalib and E. Rosenberg, *J. Cluster Sci.*, 2001, **12**, 5; M. M. Hossain, H.-M. Lin and S.-G. Shyu, *Eur. J. Inorg. Chem.*, 2001, 2655; M. Herberhold, J. Peukert, M. Kruger, D. Daschner and W. Milius, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1289; R. S. Dickson, G. D. Fallon, W. R. Jackson and A. Polas, *J. Organomet. Chem.*, 2000, **607**, 156.

2 E. W. Abel, S. K. Suresh and K. G. Orrell, *Prog. Inorg. Chem.*, 1984, **32**, 1.

3 (*a*) H. Torrens, *Coord. Chem. Rev.*, 2000, **196**, 331; (*b*) M. L. H. Green and D. K. P. Ng, *J. Chem. Soc., Dalton Trans.*, 1993, 11; (*c*) E. W. Abel, N. A. Cooley, K. Kite, K. G. Orrell, V. Sik, M. B. Hursthorse and H. M. Dawes, *Polyhedron*, 1987, **6**, 1261; (*d*) R. D. Adams, D. A. Katahira and L. W. Yang, *Organometallics*, 1982, **1**, 235; (*e*) I. B. Benson, S. A. R. Knox, P. J. Naish and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1981, 2235; (*f*) S. D. Killops and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1978, 1260; (*g*) G. Natile, L. Maresca and G. Bor, *Inorg. Chim. Acta*, 1977, **23**, 37.

4 P. M. Treichel and M. H. Tegen, *J. Organomet. Chem.*, 1988, **358**, 339; P. M. Treichel and P. C. Nakagaki, *Organometallics*, 1986, **5**, 711; J. Grobe and R. Rau, *J. Fluorine Chem.*, 1978, **11**, 265.

5 V. Küllmer and H. Vahrenkamp, *Chem. Ber.*, 1976, **109**, 1560.

6 (*a*) H. Egold, S. Klose and U. Flörke, *Z. Anorg. Allg. Chem.*, 2001, **627**, 164; (*b*) J. Grobe, J. Vetter, B. Krebs and M. Pascaly, *Z. Anorg. Allg. Chem.*, 2000, **626**, 430.

7 H. Egold and U. Flörke, *Z. Anorg. Allg. Chem.*, 2001, **627**, 2295.

8 H. Egold, D. Schwarze and U. Flörke, *J. Chem. Soc., Dalton Trans.*, 1999, 3203.

9 (*a*) C. P. Perrin and T. J. Dwyer, *Chem. Rev.*, 1990, **90**, 935; (*b*) E. W. Abel, T. P. J. Coston, K. G. Orrell, V. Sik and D. Stephenson, *J. Magn. Reson.*, 1986, **70**, 34; (*c*) J. Jeener, B. H. Meier, P. Bachmann and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.

10 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

11 (*a*) M. I. Bruce, P. J. Low, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1996, **515**, 65; (*b*) S. Top, M. Gunn, G. Jaouen, J. Vaissermann, J. C. Daran and M. J. McGlinchey, *Organometallics*, 1992, **11**, 1201; (*c*) K W. Lee and T. L. Brown, *Organometallics*, 1985, **4**, 1025; (*d*) P. O. Nubel, S. R. Wilson and T. L. Brown, *Organometallics*, 1983, **2**, 515.

12 X. Zhang, C. A. Dullaghan, E. J. Watson, G. B. Carpenter and D. A. Sweigart, *Organometallics*, 1998, **17**, 2067; C. A. Dullaghan, G. B. Carpenter, D. A. Sweigart, D. S. Choi, S. S. Lee and Y. K. Chung, *Organometallics*, 1997, **16**, 5688.

13 D. A. Vicic and W. D. Jones, *Organometallics*, 1997, **16**, 1912.

14 V. Küllmer and H. Vahrenkamp, *Chem. Ber.*, 1977, **110**, 3799; V. Küllmer and H. Vahrenkamp, *Chem. Ber.*, 1976, **109**, 1569; E. W. Abel, A. M. Atkins, B. C. Crosse and G. V. Hutson, *J. Chem. Soc. A*, 1968, 687.

15 V. Küllmer and H. Vahrenkamp, *Chem. Ber.*, 1977, **110**, 3810.

16 A. G. Orpen, HYDEX, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

17 U. Jüptner, PhD Thesis, Paderborn, Germany, 1993; E. Magnusson, *Phosphorus Sulfur*, 1986, **28**, 379.

18 E. Niecke and H. Westermann, *Synthesis*, 1988, 330.

19 G. M. Sheldrick, SHELX-97, A Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1998.