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The syntheses of novel sulfur centred spirocyclic cluster complexes starting from [$Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8$]

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[$Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8$] **1** reacted with [$Re_2(CO)_8(MeCN)_2$], [$Os_3(CO)_{11}(MeCN)$], [$Co_2(CO)_8$] and [$Fe_2(CO)_9$], respectively, by SH oxidative addition to give the spirocyclic cluster complexes [$\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S)$] **2**, [$(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Os_3(\mu\text{-}H)(CO)_{10}$] **3**, [$(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Fe_2(CO)_6(\mu_4\text{-}S)Re_2(\mu\text{-}H)(CO)_8$] **4** and [$(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Co_2(CO)_6(\mu_4\text{-}S)Re_2(\mu\text{-}H)(CO)_8$] **5** in good yields. Complexes **2**, **3** and **4** have been characterised by crystal structure analysis. Cluster complex **2** consists of two hydrido bridged dirhenium octacarbonyl units linked by a tetrahedral μ_4-S. The crystal structure of **3** shows an analogous Re_2 unit and a planar Os_3 ring linked by a tetrahedral μ_4-S. Cluster complex **4** consists of one Fe_2 and two Re_2 units linked into a chain by two tetrahedral μ_4-S bridges. The structure of **5** is similar to that of **4** and was derived from spectroscopic data and elemental analysis. The formation of **3** was shown to proceed in two steps. First the acetonitrile ligand in [$Os_3(CO)_{11}(MeCN)$] is substituted by **1** followed by SH oxidative addition giving the intermediate [$(OC)_8(\mu\text{-}H)Re_2(\mu_3\text{-}S)Os_3(\mu\text{-}H)(CO)_{11}$] **6**. Upon heating the cluster complex eliminates one equivalent of CO yielding **3** as the final product. The molecular structure of **6** has been established by single crystal X-ray analysis.

Introduction

Recently we reported the synthesis of cluster complexes of the general formula [$Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8$] (R = H or organic residue).[1] The compounds were obtained by treating [$Re_2(CO)_8(MeCN)_2$] with an excess of thiol or H_2S, respectively. The further reaction of [$Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8$] **1** with [$Re_2(CO)_8(MeCN)_2$] at 80 °C in toluene gave the spirocyclic compound [$\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S)$] **2**. Its structure was derived from spectroscopic data and elemental analysis. Now the structure of **2** has been established by single crystal X-ray analysis. Such sulfur centred spirocyclic carbonyl complexes are rare. In many compounds containing a μ_4-S ligand the sulfur caps as a four-electron donor a square planar arrangement of four metal atoms.[2] Carbonyl complexes with tetrahedral μ_4-S ligands are known for rhenium,[1] mixed rhenium and ruthenium,[3] ruthenium,[4] osmium[5] and iron[6] complexes, respectively. The majority of the above mentioned complexes were prepared either by pyrolysis[3,4,6] or photolysis.[5] As **2** was formed under mild conditions in good yield we decided to use **1** for the synthesis of new spirocyclic mixed metal complexes. The metal carbonyl complexes chosen for these syntheses were known to react with SH functions by SH oxidative addition. This is particularly known for [$Os_3(CO)_{11}(MeCN)$],[7] [$Fe_2(CO)_9$][8] and [$Co_2(CO)_8$].[9] The first cluster complex add thiols HSR to give hydrido sulfido bridged complexes of general formula [$Os_3(\mu\text{-}H)(\mu\text{-}SR)(CO)_{10}$] whereas the last two react with thiols to form sulfido bridged complexes [$Fe_2(\mu\text{-}SR)_2(CO)_6$] and polynuclear cobalt complexes, respectively. We found that **1** reacts analogously to thiols giving hydrido sulfido bridged complexes with [$Os_3(CO)_{11}(MeCN)$] and doubly sulfido bridged complexes with [$Fe_2(CO)_9$]. The reaction with [$Co_2(CO)_8$] proceeds differently to plain thiols giving doubly sulfido bridged complexes instead of polynuclear cobalt clusters.

Results and discussion

[$Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8$] **1** reacts with [$Re_2(CO)_8(MeCN)_2$] by SH oxidative addition to give the spirocyclic compound [$\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S)$] **2** in 60% yield (Scheme 1).[1] Now the structure of **2** has been confirmed by a single crystal X-ray analysis. The straightforward synthesis of **2** and the resulting good yield encouraged us to treat other metal carbonyl complexes with **1** in order to get mixed metal spirocyclic complexes.

Reaction of [$Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8$] with [$Os_3(CO)_{11}(MeCN)$]

We started our investigations with [$Os_3(CO)_{11}(MeCN)$]. Complex **1** reacts with the latter in dichloromethane at room temperature to give a yellow precipitate. If the reaction mixture is not stirred crystals of the the product are obtained. A single crystal X-ray analysis revealed the precipitate to be [$(OC)_8(\mu\text{-}H)Re_2(\mu_3\text{-}S)Os_3(\mu\text{-}H)(CO)_{11}$] **6** (Scheme 2). It was isolated in 68% yield. Apparently **6** is formed by SH oxidative addition of **1** to [$Os_3(CO)_{11}(MeCN)$]. The resulting molecule consists of a μ-H bridged Os_3 ring that is co-ordinated by a sulfur ligand bridging a dirhenium complex. The sulfur ligand co-ordinates the osmium perpendicular with respect to the plane of the Os_3 ring. The complex can be detected by IR spectroscopy during its formation, but after precipitation is insoluble in all common organic solvents (*e.g.* dichloromethane, thf, chloroform, n-hexane, acetone). Therefore the only spectroscopic data available are IR (KBr pellet) and *in situ* ^1H NMR data. As a consequence of the low symmetry of the molecule (C_s) the ν(CO) IR spectrum exhibits 12 absorption bands. ^1H NMR spectra of equimolar amounts of **1** and [$Os_3(CO)_{11}(MeCN)$] in $CDCl_3$ exhibited apart from the signals of the reagents two new resonances at high field that may be ascribed to the μ-H ligands of **6**. The resonance at δ −13.80 (Table 1) is assigned to the μ-H ligand bridging the dirhenium fragment whereas the signal at δ −16.38 belongs to the μ-H ligand bridging the Os_3 fragment. These are typical chemical shifts compared to those of similar hydrido bridged dirhenium and triosmium cluster complexes like [$Re_2(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8$] ($\delta$(μ-H) −13.87)[1,10] or [$Os_3(\mu\text{-}H)(\mu\text{-}SC_6H_4CO_2H)(CO)_{10}$] ($\delta$(μ-H) −16.8).[11] The intensity of the observed new resonances reached their maxima after 8 to 10 minutes then decreased rapidly due to precipitation of **6**. Unfortunately the two μ-H ligands were not directly located in

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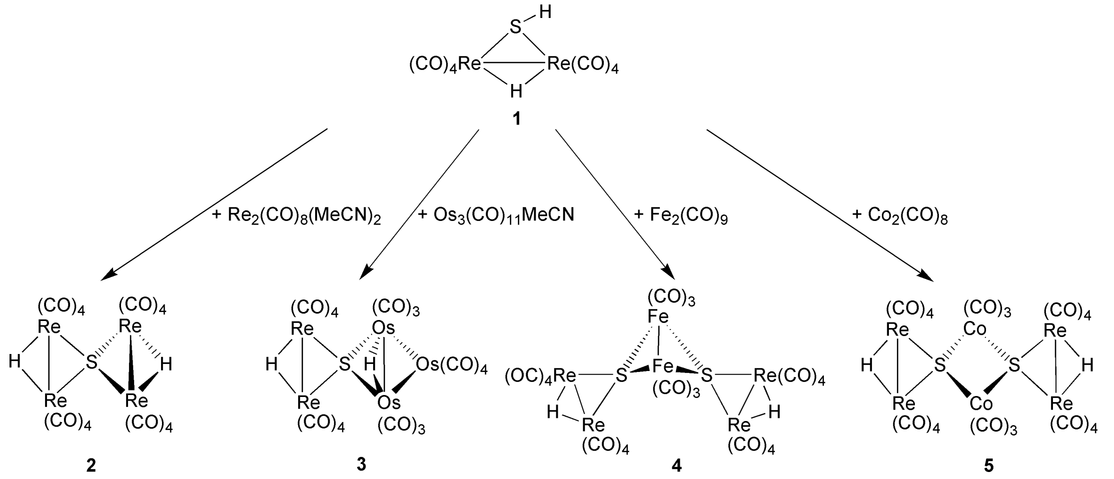
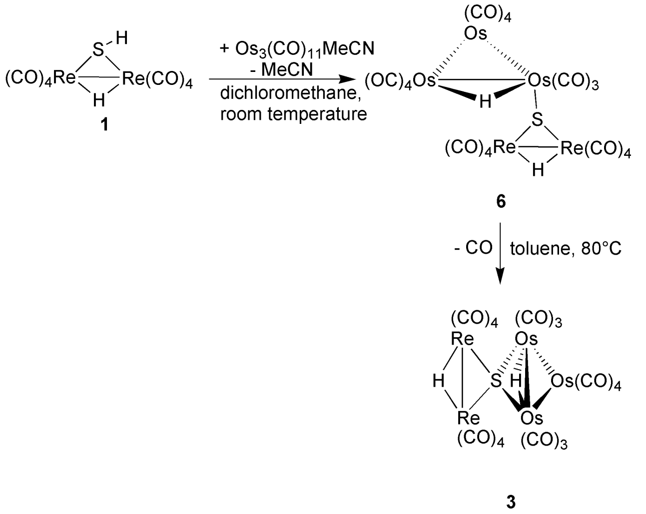
Table 1 The IR and NMR data of the cluster complexes

Complex	$\tilde{\nu}$(CO)[a]/cm^{-1}	^{1}H NMR (δ, J/Hz)[b]
2	2106w, 2094m, 2025vs, 1969m[c]	−13.56 (s, μ-H)
3	2121w, 2100m, 2096m, 2069vs, 2054s, 2023vs, 2008s, 1967m[c]	−13.57 (s, 1H, μ-H (Re)); −15.68 (s, 1H, μ-H (Os))
4	2112w, 2094m, 2063m, 2050vs, 2020m, 2004s, 1965m, 1953sh[c]	−13.63 (s, μ-H)
5	2146w, 2105m, 2094m, 2085s, 2038vs, 2006s, 1988s, 1948s[c]	−13.66 (s, μ-H)
6	2143m, 2106m, 2094s, 2083vs, 2065vs, 2034s, 2021vs, 2000vs, 1975vs, 1959vs, 1940vs, 1927vs[d]	−13.80 (s, 1H, μ-H (Re)); −16.38 (s, 1H, μ-H (Os))[e]

[a] CaF_2 optics. [b] In $CDCl_3$. [c] In thf. [d] KBr pellet. [e] *in situ* data.



Scheme 1 Reactions of compound **1** with different metal carbonyl complexes.



Scheme 2 Reaction sequence leading to complex **3**.

the crystal structure analysis of **6**. Nevertheless their existence is clearly indicated by the arrangement of the CO ligands. On heating a suspension of **6** in toluene to 80 °C one equivalent of CO is eliminated and an almost quantitative conversion into the novel spirocyclic complex $[(OC)_8(\mu\text{-H})Re_2(\mu_4\text{-S})Os_3(\mu\text{-H})(CO)_{10}]$ **3** takes place (Scheme 2). A similar sequence has been observed in the reaction of $[Os_3(CO)_{11}(MeCN)]$ with HX (X = Cl or Br). In that case the analogous intermediate $[Os_3(\mu\text{-H})(CO)_{11}X]$ (X = Cl or Br) was isolated in 50% yield. Its structure was derived from spectroscopic data. On heating in cyclohexane it lost CO to give $[Os_3(\mu\text{-H})(\mu\text{-X})(CO)_{10}]$.[12] Hence, **6** is an important intermediate in SH oxidative additions to $[Os_3(CO)_{11}(MeCN)]$. Recently another intermediate in this type of reaction has been observed by NMR spectroscopy.[13] These experiments indicated that the SH oxidative addition of plain thiols HSR (R = *o*-, *m*-, or *p*-MeC_6H_4, 2-naphthyl, Et or *t*-Bu), proceeds in at least three steps. First the acetonitrile ligand dissociates. Subsequently the thiol is added to the give substituted complex $[Os_3(CO)_{11}(HSR)]$ which contains an agostic Os–H–S interaction. Finally CO is lost giving $[Os_3(\mu\text{-H})(\mu\text{-SR})(CO)_{10}]$. The chemical shift of the agostic H was found to be at about δ −5. We were not able to detect an analogous intermediate in the reaction mixture. All ^{1}H NMR spectra recorded in the course of the reaction of $[Os_3(CO)_{11}(MeCN)]$ with **1** exhibited only resonances of the reagents and of **6**. The region between δ 0 and −13 displayed no resonances at all. We assume that an intermediate $[(OC)_{11}Os_3(\mu\text{-SH})Re_2(\mu\text{-H})(CO)_8]$ with an agostic Os–H–S is formed as well, but reacts more rapidly due to activation of the SH bond by three sulfur–metal contacts. On the other hand **6** may be stable due to intramolecular crowding hindering sulfur ligand attack on another osmium atom with its lone pair of electrons. Upon heating, however, the steric hindrance is overcome and nucleophilic attack of the sulfur on another osmium takes place giving the spirocyclic cluster complex **3**.

After separation complex **3** was obtained as a yellow solid in 97% yield. The cluster complex was characterised by ^{1}H NMR and IR spectroscopic data (Table 1) as well as by elemental analysis. In addition, its structure has been confirmed by crystal structure analysis. The infrared spectrum displays the typical ν(CO) patterns of hydrido sulfido bridged dirhenium complexes $[Re_2(\mu\text{-H})(\mu\text{-SR})(CO)_8]$ and triosmium complexes $[Os_3(\mu\text{-H})(\mu\text{-SR})(CO)_{10}]$. The ^{1}H NMR spectrum confirms the presence of two non-equivalent μ-H ligands. From comparison with other hydrido sulfido bridged dirhenium compounds[1] the downfield resonance at δ −13.57 has been assigned to the μ-H ligand bridging the dirhenium unit. Consequently the upfield signal at δ −15.68 has been assigned to the μ-H ligand bridging two osmium atoms.

Reaction of $[Re_2(\mu\text{-H})(\mu\text{-SH})(CO)_8]$ with $[Fe_2(CO)_9]$ and $[Co_2(CO)_8]$

The reaction of $[Fe_2(CO)_9]$ with thiols HSR gives the well known complexes $[Fe_2(\mu\text{-SR})_2(CO)_6]$ in good yields.[9] Therefore we decided to treat **1** with $[Fe_2(CO)_9]$ in toluene at ambient temperature. **1** reacts completely analogously to thiols giving

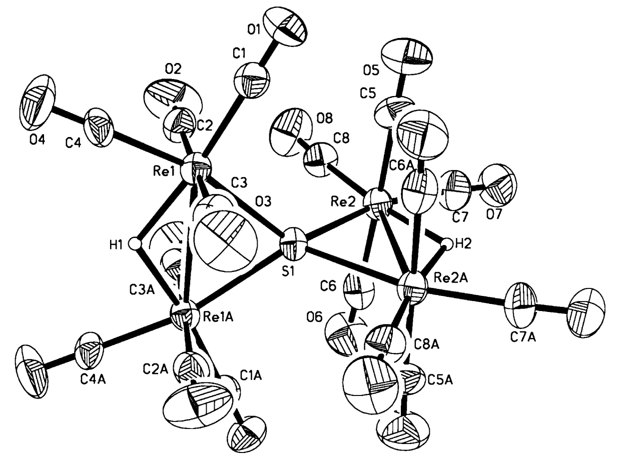


Fig. 1 Molecular structure of complex **2**. Selected bond lengths (Å) and angles (°): Re1–Re1A 3.1145(8), Re2–Re2A 3.1282(11), Re1–S1 2.479(3) and Re2–S1 2.482(3); Re1–S1–Re1A 77.84(11), Re2–S1–Re2A 78.14(11), Re1–S1–Re2 126.73(2), Re1–S1–Re2A 127.60(2), C4–Re1–Re1A 114.8(3) and C7–Re2–Re2A 114.9(4).

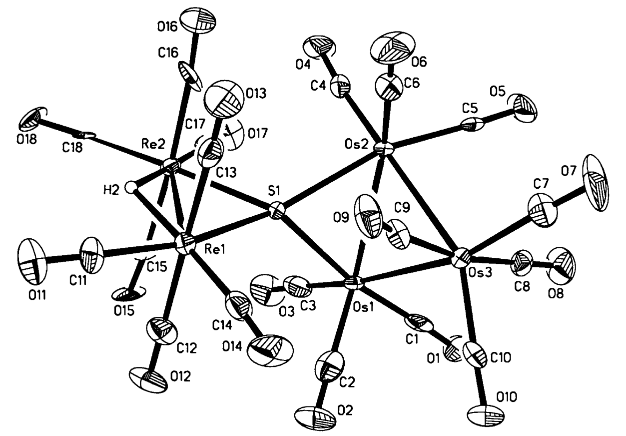


Fig. 2 Molecular structure of complex **3**. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1036(11), Re1–S1 2.494(3), Re2–S1 2.489(3), Os1–Os2 2.8637(10), Os1–Os3 2.8956(9), Os2–Os3 2.8431(9), Os1–S1 2.403(3) and Os2–S1 2.462(3); Re1–S1–Re2 77.06(8), C11–Re1–Re2 115.2(4), C18–Re2–Re1 118.6(4), Os1–S1–Os2 71.66(8), C1–Os1–Os2 115.9(4), C5–Os2–Os1 111.0(4), Re1–S1–Os1 127.84(13), Re1–S1–Os2 142.70(13), Re2–S1–Os1 125.77(13) and Re2–S1–Os2 120.13(12).

the novel spirocyclic cluster complex $[(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Fe_2(CO)_6(\mu_4\text{-}S)Re_2(\mu\text{-}H)(CO)_8]$ **4** in 40% yield. We were not able to observe any intermediates of this reaction. The ν(CO) spectrum of **4** exhibits the typical pattern of absorption bands observed for hydrido sulfido bridged dirhenium complexes[1] and three additional bands that must be assigned to the $Fe(CO)_3$ fragments. Only terminally bonded carbonyl stretching frequencies were observed. The ^1H NMR resonance of the μ-H ligands can be found at δ −13.63 and correlates well with the resonance observed for **2** at δ −13.56.

The reaction of complex **1** with $[Co_2(CO)_8]$ in toluene at 80 °C gives $[(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Co_2(CO)_6(\mu_4\text{-}S)Re_2(\mu\text{-}H)(CO)_8]$ **5** in 20% yield. As we were not able to obtain single crystals of this compound its structure (Scheme 1) was derived from spectroscopic data and elemental analysis. The IR spectrum is similar to the one observed for **4** and the ^1H NMR resonance at δ −13.66 is consistent with a hydrido sulfido bridged rhenium complex (compare discussion above). We assume that the Co_2S_2 ring is planar with no bonding Co–Co interaction as each sulfido bridge must be regarded as a three electron donor with respect to the dicobalt fragment. Similar molecules $Co_2(\mu\text{-}SR)_2(CO)_6$ were reported to exist,[13] but attempts to reproduce their synthesis failed. Instead multinuclear cluster compounds have been obtained containing doubly and triply bridging SR groups.[14] It is likely that the formation of **5** is possible because **1** has only one lone pair of electrons at the bridging sulfur atom left, decreasing the reactivity of sulfur with respect to the cobalt carbonyl.

Molecular structures of complexes 2, 3, 4 and 6

The structures of spirocyclic sulfur complexes are known from some examples, see *e.g.* refs. 3*a*,*b*,5*c*,*d* and 6 and literature cited therein, but **2** (Fig. 1) is the first homonuclear rhenium cluster compound of this type. The μ_4-S center is tetrahedrally co-ordinated by two pairs of metal–metal bonded Re_2 units. The non-metal ligand sphere of each Re atom comprises four terminal CO groups and a μ-H ligand, which bridges the Re–Re bond. Thus each rhenium reaches a slightly distorted octahedral non-metal co-ordination. With respect to the Re–Re vector the carbonyl groups at each Re_2 unit are in eclipsed position with C–Re–Re–C torsion angles in the range from 1.2(6) to 8.6(6)°. The μ-H ligands were located from ΔF maps and refined. They are positioned in the planes of the Re_2S units each midway between the equatorial CO groups 4/4A and 7/7A, respectively, which show the typical large C–Re–Re angles of 114.8(3) and 114.9(4)°. The central μ_4-S atom lies on a crystallographic twofold axis and the dihedral angle between the two Re_2S planes is 90.9°. The Re–Re (3.1145(8) and 3.1282(11) Å) and Re–S (2.479(3) and 2.482(3) Å) bond lengths as well as the Re–S–Re angles of 77.84(11) and 78.14(11)°, respectively, compare well with those parameters known from the related cluster complex $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{14}]$ (Re–Re 3.129(2), Re–S 2.464(4) and 2.472(3) Å).[3a] Complex $[Re_2Ru_2(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)(C_5H_4NS)(CO)_{13}]$ with no Re–Re bond shows somewhat longer Re–S bond lengths from 2.508(2) to 2.553(2) Å.[3b]

Complex **3** (Fig. 2) is closely related to the structure of **2**, but with one $Re_2(\mu\text{-}H)(CO)_8$ unit replaced by a triangular $Os_3(\mu\text{-}H)(CO)_{10}$ part with Os–Os bonds. The two osmium atoms bonded to the μ_4-S are attached to three terminal CO groups each and to the common Os3 atom. The latter has four terminal CO groups as non-metal ligands. The μ-H ligand which bridges the Os1–Os2 bond could not be determined, but is ascertained from ^1H NMR data. Moreover the position of both the CO groups 1 and 5 with C–Os–Os angles of 115.9(4) and 111.0(4)° indicate its position in the Os_2S plane in correspondence to the second μ-H ligand which bridges the Re–Re bond as in **2** and that was located from the ΔF map. The dihedral angle between the two Re_2S and Os_2S planes is 80.2° and the Os_3 and Os_2S planes enclose an angle of 68.3°. The Re–Re and Re–S bond lengths of 3.1036(11) and 2.494(3) (Re1) and 2.489(3) Å (Re2), respectively, and the Re–S–Re angle of 77.06(8)° are close to the corresponding values of **2**. The Os–S (Os1 2.430(3), Os2 2.462(3) Å) and Os–Os bond lengths (Os1–Os 2.8637(10), Os2–Os 2.8431(9), Os1–Os 2.8956(9) Å) and the Os–S–Os angle of 71.66(8)° are comparable to those of $[Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NPh)_2(CO)_{18}]$[5d] or $[Os_6(\mu_4\text{-}S)(\mu_3\text{-}S)(CO)_{20}]$.[5c]

The basic structure type of the heteronuclear iron rhenium cluster **4** (Fig. 3) is known from $[Os_6(\mu_4\text{-}S)_2(\mu\text{-}HC{=}NPh)_2(CO)_{18}]$.[5d] The central molecular fragment is a butterfly Fe_2S_2 core with a Fe_2S/SFe_2 dihedral angle of 109.2° and each Fe atom linked to three terminal CO ligands. These show an ecliptic arrangement viewed along the Fe–Fe bond; the C9–Fe1–Fe2–C12 torsion angle is 13.9(9)°. The Fe–Fe bond length is 2.539(2) Å and the Fe–S pattern shows alternating short and long distances of Fe1–S1 2.251(3), S1–Fe2 2.308(3), Fe2–S2 2.262(3) and S2–Fe1 2.303(3) Å. Both μ_4-S atoms are additionally linked to $Re_2(\mu\text{-}H)(CO)_8$ units which exhibit the same geometry as described for **2**. The Re–Re bond lengths Re1–Re2 3.0863(9) and Re3–Re4 3.0925(8) Å are slightly shorter than those of **2** but the Re–S distances Re1–S1 2.487(2), Re2–S1 2.485(2), Re3–S2 2.488(2), Re4–S2 2.484(2) Å are identical. The resulting dihedral angles are $Fe_2S1/S1Re_2$ 76.8 and $Fe_2S2/S2Re_2$ 100.0°,

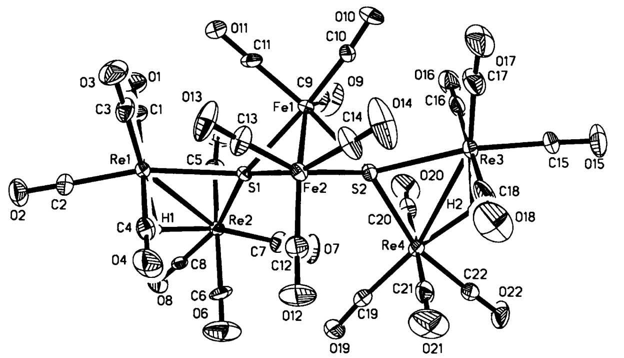


Fig. 3 Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°): Re1–Re2 3.0863(9), Re1–S1 2.487(2), Re2–S1 2.485(2), Re3–Re4 3.0925(8), Re3–S2 2.488(2), Re4–S2 2.484(2), Fe1–Fe2 2.5392(19), Fe1–S1 2.251(3), Fe1–S2 2.303(3), Fe2–S1 2.308(3) and Fe2–S2 2.262(3); Re1–S1–Re2 76.73(7), Re3–S2–Re4 76.92(7), Fe1–S1–Fe2 67.68(8), Fe1–S2–Fe2 67.59(8), Re1–S1–Fe1 130.25(10), Re1–S1–Fe2 121.20(10), Re2–S1–Fe1 127.52(10), Re2–S1–Fe2 143.71(10), Re3–S2–Fe1 120.93(10), Re3–S2–Fe2 128.34(10), Re4–S2–Fe1 142.14(11), Re4–S2–Fe2 130.41(11), C2–Re1–Re2 115.9(3), C8–Re2–Re1 112.7(3), C15–Re3–Re4 115.0(3) and C22–Re4–Re3 111.5(3).

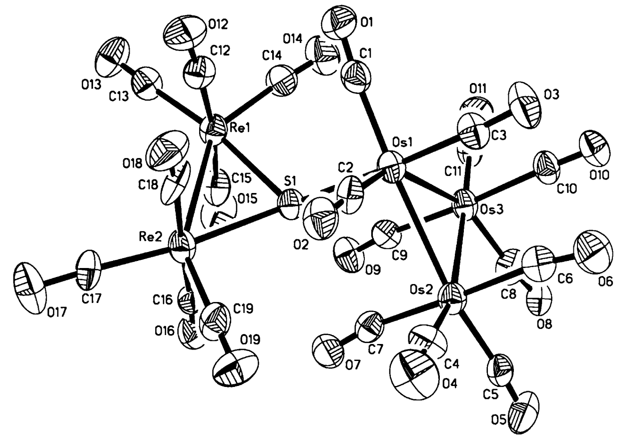


Fig. 4 Molecular structure of complex **6**. Selected bond lengths (Å) and angles (°): Re1–Re2 3.0900(13), Re1–S1 2.482(5), Re2–S1 2.477(5), Os1–Os2 2.8979(13), Os1–Os3 3.0326(12), Os2–Os3 2.8956(12) and Os1–S1 2.478(5); Re1–S1–Re2 77.08(14), Re1–S1–Os1 122.9(2), Re2–S1–Os1 127.6(2), C13–Re1–Re2 122.1(7), C17–Re2–Re1 117.4(8), C1–Os1–Os3 114.7(6) and C11–Os3–Os1 119.5(8).

so the Re_2S planes are not parallel. The two μ-H ligands were located from ΔF maps and refined.

Complex **6** (Fig. 4) is a new type of heteronuclear cluster complex which exhibits a μ_3-S atom that connects the discussed $Re_2(\mu\text{-}H)(CO)_8$ unit with a triangular $Os_3(\mu\text{-}H)(CO)_{11}$ fragment. Of the latter Os2 and Os3 are attached to four terminal CO groups each which show an ecliptic arrangement viewed along the Os2–Os3 bond with torsion angles in the range of 0.1 to 0.6(9)°. Os1 has three terminal CO groups and is connected to the μ_3-S bridging atom which is in axial position relative to the Os_3 ring. Both μ-H ligands could not directly be located but are ascertained from ^1H NMR data. As indicated by the C–Re–Re angles of the equatorial CO groups 13 (122.1(7)°) and 17 (117.4(8)°) the μ-H atom bridging the Re–Re bond lies in the SRe_2 plane, consistent with the results for **2**, **3** and **4**. Inspection of the equatorial CO groups of the Os_3 unit and the related C–Os–Os angles shows that the remaining μ-H atom is likely to bridge the Os1–Os3 bond because the angles C2–Os1–Os2 (89.6(7)°), C4–Os2–Os1 (98.1(7)°), C5–Os2–Os3 (99.6(7)°) and C8–Os3–Os2 (87.7(7)°) are mostly rectangular but C1–Os1–Os3 (114.7(6)°) and C11–Os3–Os1 (119.5(8)°) are widened in the usual manner. Additionally, the Os1–Os3 bond length of 3.0326(12) Å is clearly elongated compared to the equally short Os1–Os2 2.8979(13) Å and Os2–Os3 2.8956(12) Å distances. This also is in accordance with the expected lengthening of μ-H supported metal–metal bonds. The three metal–sulfur bonds are of equal length (Re1 2.482(5), Re2 2.477(5), Os1 2.478(5) Å) and the Os1–S1–Re angles of 122.9(2) (Re1) and 127.6(2)° (Re2) show an almost linear arrangement along the S–Os vector. The corresponding torsion angle X–S–Os1–Y with X = the midpoint of Re1–Re2 and Y = the midpoint of Os2–Os3 is 177.1°. A somewhat related structure but with additional bridging pattern is realised with the homonuclear osmium compound $[(OC)_6Os_2(\mu_3\text{-}S)(\mu_4\text{-}S)Os_4(CO)_{14}]$.[5c]

Experimental

General conditions

All reactions were performed in solvents free of oxygen 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).

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).

Starting materials

The compounds $[Fe_2(CO)_9]$ and $[Co_2(CO)_8]$ were purchased from Fluka and used as received. The complexes $[Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8]$,[1] $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S)]$[1] and $[Os_3(CO)_{11}(MeCN)]$ [12] were prepared according to literature methods.

Preparations

$\boldsymbol{[(OC)_8(\mu\text{-}H)Re_2(\mu_3\text{-}S)Os_3(\mu\text{-}H)(CO)_{11}]}$ **6.** $[Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8]$ **1** (69 mg, 0.108 mmol) and one equivalent of $[Os_3(CO)_{11}(MeCN)]$ (100 mg, 0.109 mmol) were dissolved in 15 ml of dichoromethane. A yellow precipitate was formed within 15 minutes. This was collected by filtration and washed three times with 5 ml of dichloromethane. The resulting yellow powder is pure compound **6**. Yield: 68% (112 mg) (Found: C, 15.13; H, 0.23. $C_{19}H_2O_{19}Os_3Re_2S$ requires C, 15.12; H, 0.13%).

$\boldsymbol{[(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Os_3(\mu\text{-}H)(CO)_{10}]}$ **3.** A yellow suspension of $[(OC)_8(\mu\text{-}H)Re_2(\mu_3\text{-}S)Os_3(\mu\text{-}H)(CO)_{11}]$ **6** (100 mg, 0.066 mmol) in 15 ml of toluene was heated to 80 °C. All the starting material reacted within 20 minutes giving a clear orange solution. Filtration through silica gel and removal of the solvent afforded yellow compound **3** in 97% yield (95 mg) (Found: C, 14.68; H, 0.10. $C_{18}H_2O_{18}Os_3Re_2S$ requires C, 14.60; H, 0.14%).

$\boldsymbol{[(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Fe_2(CO)_6(\mu_4\text{-}S)Re_2(\mu\text{-}H)(CO)_8]}$ **4.** $[Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8]$ **1** (100 mg, 0.159 mmol) and $[Fe_2(CO)_9]$ (50 mg, 0.137 mmol) were dissolved in 25 ml of toluene and stirred at room temperature for two hours. Removal of the solvent and TLC (eluent dichloromethane–*n*-hexane (1 : 1)) gave pure compound **4**. Recrystallisation from dichloromethane–*n*-hexane afforded dark red **4** in 40% yield (58 mg) (Found: C, 16.67; H, 0.12. $C_{22}H_2Fe_2O_{22}Re_2S_2$ requires C, 17.17; H, 0.13%).

$\boldsymbol{[(OC)_8(\mu\text{-}H)Re_2(\mu_4\text{-}S)Co_2(CO)_6(\mu_4\text{-}S)Re_2(\mu\text{-}H)(CO)_8]}$ **5.** $[Re_2(\mu\text{-}H)(\mu\text{-}SH)(CO)_8]$ **1** (100 mg, 0.159 mmol) and $[Co_2(CO)_8]$ (27 mg, 0.079 mmol) were dissolved in 25 ml of toluene and stirred at 80 °C. The solution turned brown within 5 minutes. After one hour it was cooled to room temperature. Removal of the solvent gave a dark brown residue which was worked up by TLC (eluent acetone–*n*-hexane (1 : 1)) giving yellow compound **5** (24 mg) in 20% yield (Found: C, 17.40; H, 0.23. $C_{22}H_2Co_2O_{22}Re_2S_2$ requires C, 17.10; H, 0.13%).

Table 2 Crystallographic data for compounds **2**, **3**, **4** and **6**

	2	**3**	**4**	**6**
Formula	$C_{16}H_2O_{16}Re_4S$	$C_{18}H_2O_{18}Os_3Re_2S\cdot 0.5CHCl_3$	$C_{22}H_2Fe_2O_{22}Re_4S_2\cdot CHCl_3$	$C_{19}H_2O_8Os_3Re_2S$
M	1227.0	1540.9	1658.2	1509.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$
T/K	293(2)	203(2)	193(2)	203(2)
a/Å	17.424(2)	35.480(9)	14.214(5)	8.805(2)
b/Å	9.424(1)	11.534(2)	18.351(4)	28.614(6)
c/Å	16.739(3)	16.023(6)	15.578(3)	11.870(2)
β/°	112.03(2)	111.67(2)	107.49(2)	104.12(1)
U/Å^3	2547.9(6)	6094(3)	3875(2)	2900(1)
Z	4	8	4	4
μ(Mo-Kα)/mm^{-1}	19.09	20.66	13.57	21.56
Reflections measured/unique	3606/2932	8059/6999	10562/8891	6354/6144
$R1/wR2$	0.035/0.078	0.042/0.090	0.044/0.113	0.053/0.166

Crystal structure determinations

Pertinent crystallographic data for compounds **2**, **3**, **4** 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 were monitored after every 400 reflections. **2**, **4** and **6** showed a decrease of 2–3% in intensities which were corrected accordingly. All intensities were corrected for Lorentz-polarisation effects and absorption *via* psi-scans. The structures were solved by direct and conventional Fourier methods. Full-matrix least-squares refinement based on F^2. All but hydrogen atoms were refined anisotropically. The μ-H atom positions H1, H2 of structure **2**, H2 of **3** and H1, H2 of **4** were determined from ΔF maps and refined. The μ-H atoms of **6** were not located and not included in the refinement. Program used for calculations: SHELX 97.[15]

CCDC reference number 186/2220.

See http://www.rsc.org/suppdata/dt/b0/b007148j/ for crystallographic files in .cif format.

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