DALTON
FULL PAPER

The reaction of $[Re_2(CO)_8(MeCN)_2]$ with thiols. Formation of hydrido sulfido bridged dirhenium cluster complexes $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ (R = H, *n*-Bu, Cy, Ph, C_6H_4F-*p*, C_6F_5 or 2-naphthyl)

Hans Egold,* Detlef Schwarze and Ulrich Flörke

Anorganische und Analytische Chemie der Universität Paderborn, Fachbereich 13,
Chemie und Chemietechnik, Warburger Straße 100, D-33098, Paderborn, Germany.
E-mail: he@chemie.uni-paderborn.de

Received 25th June 1999, Accepted 23rd July 1999

The complex $[Re_2(CO)_8(MeCN)_2]$ **1** reacted with thiols or H_2S, respectively, by SH oxidative addition in toluene at 80 °C to give hydrido sulfido bridged dirhenium complexes of the general formula $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ (R = H **2a**, *n*-Bu **2b**, Cy **2c**, Ph **2d**, C_6H_4F-*p* **2e**, C_6F_5 **2f** or 2-naphthyl **2g**) in 60 to 80% yield. Complexes **2c** and **2g** have been characterised by crystal structure analysis. Complex **2a** undergoes reaction with another equivalent of **1** to form the novel spirocyclic complex $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4S)]$ **3**. In order to demonstrate the acidity of the μ-H ligand **2g** was deprotonated by the base 1,8-diazabicyclo[5.4.0]undec-7-ene to give the anion $[Re_2(\mu\text{-}S(2\text{-}naph))(CO)_8]^-$ $\mathbf{4}^-$ (naph = naphthyl) which can be isolated as its PPh_4^+ salt. This reacts with one equivalent of $[MCl(PPh_3)]$ (M = Au, Ag or Cu) to give the novel heteronuclear cluster complexes $[Re_2(MPPh_3)(\mu\text{-}S(2\text{-}naph))(CO)_8]$ (M = Au **5a**, Ag **5b** or Cu **5c**) and PPh_4Cl. The molecular structures of **5a** and **5b** have been established by single crystal X-ray analysis.

Introduction

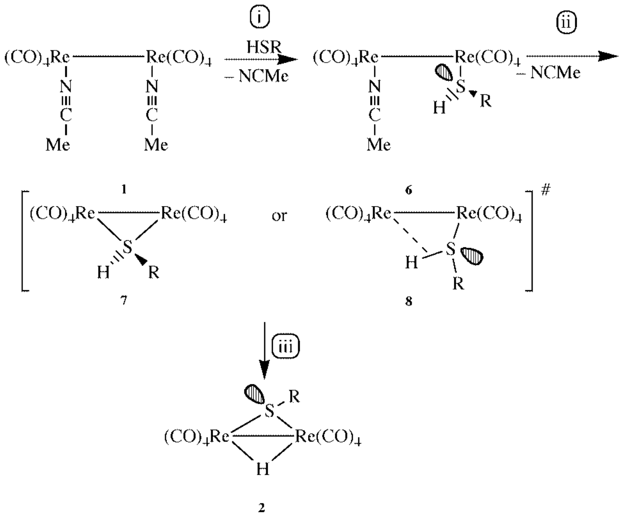
Rhenium complexes of the general formula $[Re_2(\mu\text{-}H)(\mu\text{-}Y)(CO)_8]$ (Y = PR_2,[1] Cl, I,[2] η^2-pyridyl,[3] η^2-C≡CR,[4] η^2-CH=CRR′,[5] C(R)O[6]) are well known in organometallic chemistry. Especially the reactivity of the hydrido phosphido bridged complexes has been studied intensively over the last years with respect to cluster synthesis[7] and cluster catalysis.[8] In this context it is most surprising that so far only two hydrido sulfido bridged dirhenium complexes $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ (R = 3-methoxycarbonyl-6-methylquinoline or CH_2-μ-S$[Re_2(\mu\text{-}H)(CO)_8]$) are known.[9] The procedures leading to these two compounds do not allow the preparation of other hydrido sulfido bridged dirhenium complexes. Therefore we decided to search for a more generally applicable synthetic route to this class of complexes. As the corresponding complexes $[M_3(\mu\text{-}H)(\mu\text{-}SR)(CO)_{10}]$ (M = Ru or Os)[10] are easily obtained from the dinitrile precursors $[M_3(CO)_{10}(MeCN)_2]$ and one equivalent of thiol we decided to perform a similar reaction sequence using the precursor $[Re_2(CO)_8(MeCN)_2]$ **1**.

In this paper we report the preparation of $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ **2** from the reaction of complex **1** with two equivalents of thiol HSR in toluene at 80 °C. The acidity of the μ-H ligand was demonstrated by the reaction of $[Re_2(\mu\text{-}H)(\mu\text{-}S(2\text{-}naph))(CO)_8]$ **2g** with the base dbu (1,8-diazabicyclo-[5.4.0]undec-7ene) giving the anion $[Re_2(\mu\text{-}S(2\text{-}naph))(CO)_8]^-$ $\mathbf{4}^-$ (naph = naphthyl). This anion reacts with $MCl(PPh_3)$ (M = Cu, Ag or Au) to give the novel trinuclear cluster complexes $[Re_2(MPPh_3)(\mu\text{-}S(2\text{-}naph))(CO)_8]$ **5**.

Results and discussion

Preparation and characterisation of $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$

Complex **1** in toluene reacts with thiols HSR (R = H, *n*-Bu, Cy, Ph C_6H_4F-*p* or C_6F_5) at 80 °C to give the hydrido sulfido bridged dirhenium complexes $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ **2** (Scheme 1) in 60 to 80% yield. The reaction was monitored by IR spectroscopy by following the disappearance of the *ν*(CO) absorption bands due to **1**. None of the expected intermediate compounds like $[Re_2(CO)_8(MeCN)(HSR)]$ **6** or $[Re_2(\mu\text{-}HSR)(CO)_8]$ **7** could be detected. In general, an excess of the thiol (usually 2 equivalents) was used as stoichiometric amounts led to slightly lower yields. After separation by PLC (PLC = preparative layer chromatography) the complexes were obtained as colourless air-stable solids which may be crystallised from chloroform–*n*-pentane. All new compounds were characterised by ^1H NMR and IR data (Table 1) as well as by elemental analysis. Moreover, the structures of **2c**, **2d**[11] and **2g** have been determined by crystal structure analysis. The new cluster complexes exhibit in thf or dichloromethane, respectively, a characteristic *ν*(CO) IR spectrum consisting of 5 absorption bands. Owing to the low symmetry of the complexes (C_s) 8 bands are expected on group theoretical arguments. Therefore an IR spectrum of $[Re_2(\mu\text{-}H)(\mu\text{-}SCy)(CO)_8]$ **2c** in the highly resolving solvent cyclopentane was measured. Now the expected 8 *ν*(CO) bands were observed. The ^1H NMR spectra show high field signals at about *δ* −14 which must be attributed to the μ-H



Scheme 1 Proposed reaction mechanism.

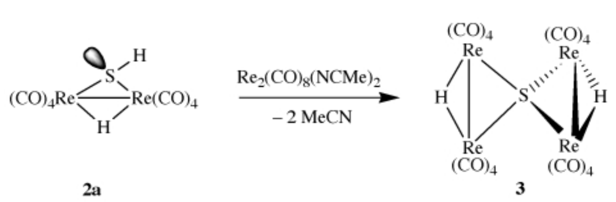
Table 1 The IR and NMR data of the cluster complexes

Complex	$\tilde{\nu}$(CO)[a]/cm^{-1}	NMR (δ, J/Hz)[a]	
		^{1}H	^{31}P
1	2069w, 2013vs, 1967m, 1956m, 1930m, 1907vs[c]	2.49 (s, Me)	
2a	2116w, 2092m, 2019vs, 1998s, 1959 m[c]	−14.36 (s, 1 H, μ-H); −0.47 (s, 1 H, SH)	
2b	2114w, 2089m, 2015vs, 1998s, 1959m[c]	−14.06 (s, 1 H, μ-H); 0.99 (t, $^3J_{HH}$ = 7.3, 3 H, CH_3); 1.48–1.60 (m, 2 H, CH_2); 1.71–1.81 (m, 2 H, CH_2); 2.85 (t, $^3J_{HH}$ = 7.4, 2 H, SCH_2)	
2c	2112m, 2089s, 2072w, 2014s, 2004s, 1997s, 1968vs, 1935w[d] 2112m, 2089s, 2017vs, 1994 (sh), 1955 m[c]	−14.10 (s, 1 H, μ-H); 1.29–2.39 (m, 11 H, Cy)	
2d	2118w, 2095s, 2022vs, 1999s, 1964s[e]	−13.87 (s, 1 H, μ-H); 7.18–7.29 (m, 3 H, Ph); 7.56 (d, $^3J_{HH}$ = 7.7, 2 H, Ph)	
2e	2118w, 2094s, 2021vs, 2002s, 1959 m[c]	−13.86 (s, 1 H, μ-H); 6.96–7.02 (m, 2 H, C_6H_4); 7.49–7.54 (m, 2 H, C_6H_4)	
2f	2119w, 2096m, 2023vs, 2008s, 1975 m[c]	−13.82 (s, μ-H)	
2g	2116w, 2094m, 2021vs, 2000s, 1959 m[c]	−13.81 (s, 1 H, μ-H); 7.27–7.95 (m, 6H, naph); 7.96 (s, 1 H, H^1(naph))	
3	2106w, 2094m, 2025vs, 1969 m[c]	−13.56 (s, μ-H)	
PPh_4^+ salt of **4**	2058m, 2000vs, 1957vs, 1940m, 1921m, 1984s, 1882s[c]	7.25–7.88 (m, Ph, naph)	23.8 (s, PPh_4^+)
5a	2089vw, 2058s, 2000vs, 1965m, 1936s[c]	7.22–7.97 (m, Ph, naph)	77.2 (s, PPh_3)
5b	2083vw, 2048vs, 1998s, 1955m, 1923s[c]	7.27–7.96 (m, Ph, naph)	21.2 (d, $J_{Ag^{107/109}P}$ = 363, PPh_3)
5c	2080vw, 2044m, 1990vs, 1956m, 1921s[c]	7.39–7.89 (m, Ph, naph)	8.0 (s, PPh_3)

[a] CaF_2 optics. [b] In $CDCl_3$. [c] In thf. [d] In cyclopentane. [e] In CH_2Cl_2.

ligands. Their chemical shift is typical for hydrido bridged dirhenium carbonyl complexes.[1–5] In this case the chemical shifts of the μ-H ligands correlate well with the electronic properties of the residue R. For electron withdrawing residues (R = Ph **2d**, C_6H_4F-*p* **2e**, C_6F_5 **2f** or 2-naphthyl **2g**) attached at the sulfido bridge the resonances are around δ −13.85 and for electron donating residues (R = *n*-Bu **2b** or Cy **2c**) they are shifted to high field at δ −14.1. As a consequence of the big difference in electronegativities between sulfur and hydrogen in case of R = H **2a** the strongest high field shift with δ −14.36 is observed. The resonance of the hydrogen bound to the sulfido bridge in **2a** can be found at δ −0.47. This is a typical chemical shift compared to those of other SH bridged dirhenium carbonyl complexes like $[Re_2(\mu\text{-}SH)_2(CO)_8]$ (δ(H) −0.89)[12] or $[Re_2(\mu\text{-}SH)_3(CO)_6]^-$ (δ(H) −0.78).[11]

On heating complex **2a** and 1.5 equivalents of **1** in toluene at 80 °C the spirocyclic compound $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S)\}$ **3** is formed in 54% yield (Scheme 2). Here the product is formed by oxidative addition of the SH function of **2a** to **1**. The ^{1}H NMR spectrum of **3** exhibits only the characteristic high field resonance of the two equivalent μ-H ligands at δ −13.56. The *ν*(CO) IR spectrum is very similar to those of the compounds of type **2** and the microanalytical data are in accordance with the proposed structure.



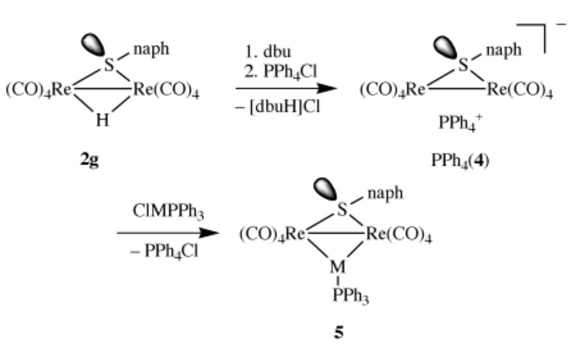
Scheme 2 Formation of complex **3**.

Mechanistic aspects

We propose the following mechanism for the formation of the new compounds of type **2** (Scheme 1). First (step i) one of the acetonitrile ligands is substituted by the thiol giving the intermediate $[Re_2(CO)_8(MeCN)(HSR)]$ **6**. We were not able to detect **6** by IR spectra of the reaction mixtures. Each spectrum exhibited only the *ν*(CO) bands of **1** and **2**. Now the second nitrile ligand is eliminated (step ii) and the intermediate **7** or **8**, respectively, is formed. A thiol bridged Re–Re bond as in **7** has not been observed yet, but similar compounds with cyclic thioethers bridging a Re–Re bond like $[Re_3(\mu\text{-}3,3\text{-}DMT)(\mu\text{-}H)_3(CO)_{10}]$ (3,3-DMT = 3,3-dimethylthietane) are known.[13] On the other hand **7** cannot be the intermediate in the reaction between **2a** and **1** as the sulfido bridge in **2a** has only one free electron pair left. In this case the intermediate **8** with a coordinated S–H bond may be formed. For plain thiols it is likely that both intermediates **7** and **8** contribute to the formation of **2**. Finally (step iii) the S–H bond is broken and the products **2** are formed.

Deprotonation and reactions with metallic electrophiles

The μ-H ligand in $[Re_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_8]$ can easily be deprotonated by the base dbu giving the anions $[Re_2(\mu\text{-}PR_2)(CO)_8]^-$.[14] In order to find out if compounds **2** react similarly **2g** in thf was treated with an excess of the base dbu for four hours (Scheme 3). The initially colourless solution turned deep yellow as the anion $[Re_2(\mu\text{-}S(2\text{-}naph)(CO)_8]^-$ **4**$^-$ is formed. In the presence of PPh_4Cl **4**$^-$ can be precipitated from a methanol–water mixture to give the pure PPh_4^+ salt. As expected its ^{1}H NMR spectrum exhibits no signal at high field. The IR spectrum shows 7 *ν*(CO) absorption bands. In comparison to **2g** the



Scheme 3 Deprotonation and subsequent metallation of complex **2g** (naph = 2-naphthyl).

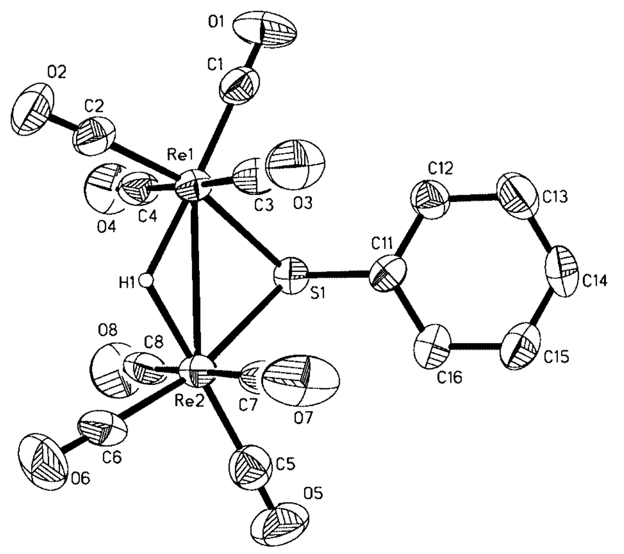


Fig. 1 Molecular structure of complex **2c**. Hydrogen atoms omitted except μ-H. Selected bond lengths (Å) and angles (°): Re1–Re2 3.0934(10), Re1–S1 2.471(3), Re2–S1 2.468(3) and S1–C11 1.817(10); Re1–S1–Re2 77.56(7), S1–Re1–Re2 51.18(6) and S1–Re2–Re1 51.26(6).

bands are significantly shifted to lower wavenumbers in accordance with the anionic nature of the cluster complex. The PPh_4^+ salt reacts easily with the coin metal complexes $[MCl(PPh_3)]$ (M = Au, Ag or Cu) in chloroform to give the novel trinuclear clusters $[Re_2(MPPh_3)(\mu\text{-}S(2\text{-naphthyl}))(CO)_8]$ **5** (M = Au **5a**, Ag **5b** or Cu **5c**) and PPh_4Cl. Their spectroscopic properties are comparable to those of $[Re_2(MPPh_3)(\mu\text{-}PR_2)(CO)_8]$ (M = Au, Ag or Cu; R = Ph or Cy).[15] In both cases the IR spectrum consists of a similar pattern of 5 *ν*(CO) bands. Besides the ^{31}P chemical shift of the PPh_3 ligands is similar, {$[Re_2(MPPh_3)(\mu\text{-}PCy_2)(CO)_8]$ *δ* (PPh_3) 82.6 (M = Au), 24.4 (Ag) or 3.9 (Cu)}. The structures of **5a** and **5b** were confirmed by X-ray diffraction analysis.

Molecular structures of complexes 2c, 2g, 5a and 5b

Complex **2c** (Fig. 1) is a dinuclear μ-H, μ-S bridged rhenium carbonyl cluster compound with one cyclohexyl group attached to the S atom. The molecular structure is closely related to that of the homologous manganese compound $[Mn_2(\mu\text{-}H)(\mu\text{-}SPh)(CO)_8]$.[16] In **2c** each Re atom attains a slightly distorted octahedral co-ordination sphere through four terminal carbonyl ligands and the common bridging hydrogen and sulfur atoms. The CO groups at both rhenium centers show an ecliptic arrangement, the largest C–Re–Re–C torsion angle being 4.7(2)° for groups 2 and 5. The position of the μ-H atom was located from the ΔF map and refined. The resulting four membered central Re_2HS ring is almost planar with equal Re–H bond lengths (1.82(7) and 1.81(10) Å) as well as equal Re–S ones (2.471(3) and 2.468(3) Å). The metal–metal distance of 3.093(1) Å clearly corresponds to a single bond which is in accordance with the 18 electrons count for each metal. This bond length is nearly the same as that of 3.0854(8) Å in the μ-H, μ-S bridged dirhenium cluster $[Re_2(\mu\text{-}H)(\mu\text{-}SR)(CO)_8]$ (R = 3-methoxycarbonyl-6-methylquinoline)[9] or the average 3.089(1) Å in $(OC)_8(\mu\text{-}H)(Re_2)$ $(\mu\text{-}S(CH_2)\mu\text{-}S)Re_2(\mu\text{-}H)(CO)_8]$.[9]

Complex **2g** (Fig. 2) exhibits in principle the same molecular structure as that of **2c** but the ligand attached to the μ-S atom is now a naphthyl group. This substitution impinges only marginally on the geometric parameters. The Re–Re bond length of 3.0909(8) Å is the same and the Re–S distances of 2.478(3) and 2.483(3) Å tend to be somewhat larger than those in **2c**.

In complex **5b** (Fig. 3) the bridging hydrogen atom of **2g** is substituted by an $AgPPh_3$ group. This leads to some distortion of the molecule with C–Re–Re–C torsion angles which now range from 7.8(2) to 13.2(2)° and with a prominent rotation of the plane of the naphthyl ligand along the C41–S axis. The latter is manifested from the torsion angle X–S–C41–C42 of 46.4(4)° where X is the centre of the Re–Re bond, whereas in **2g** this torsion angle is 95.3(7)°. However, these distortion effects may well be due to intermolecular packing repulsions from the bulky triphenylphosphine and naphthyl groups. The central Re_2AgS ring is nearly planar with a dihedral angle SRe_2/Re_2Ag of 3.4(1)°. The Re–Re bond length of 3.1077(8) Å is slightly enlarged compared to that of **2g** but clearly shorter than 3.190(1) Å of the related phosphido bridged compound $[Re_2(AgPPh_3)(\mu\text{-}PCy_2)(CO)_8]$.[17] The Re–S distances (2.464(1) and 2.473(1) Å) are comparable with those of **2c** and **2g** and the Ag–Re1 bond length (2.8199(9)Å) is distinctly shorter than Ag–Re2, 2.8476(6) Å. The exocyclic P–Ag–Re angles of 147.14(4)° (Re1) and 138.05(4)° (Re2) also differ markedly, the smaller angle being opposite to the shorter Ag–Re bond.

Complex **5a** (Fig. 4) has the same molecular structure as **5b** with Ag substituted by Au. As a consequence it shows similar C–Re–Re–C torsion angles (7.9(2) to 12.6(2)°) and orientation of the naphthyl group with an X–S–C41–C42 torsion angle of 47.9(2)° (X = centre of Re–Re bond). The Re_2AuS ring is planar and the increased Re–Re bond length of 3.1356(7) Å as well as the different Au–Re1 (2.7853(8) Å) and Au–Re2 bond lengths (2.8110(7) Å) reflect the influence of the Au atom. Again there are different exocyclic P-Au-Re angles of 139.18(6)° (Re2) and 148.14(6)° (Re1) and the smaller angle is opposite to the shorter Au–Re bond. These latter observations are also valid for

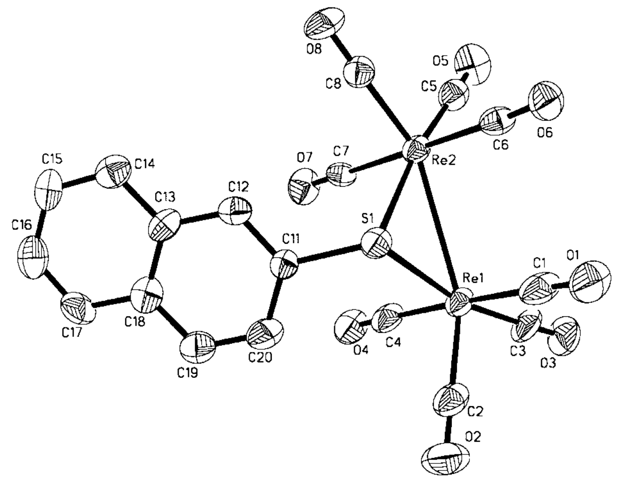


Fig. 2 Molecular structure of complex **2g**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Re1–Re2 3.0909(8), Re1–S1 2.478(3), Re2–S1 2.483(3) and S1–C11 1.808(9); Re1–S1–Re2 77.07(8), S1–Re1–Re2 51.54(6) and S1–Re2–Re1 51.39(6).

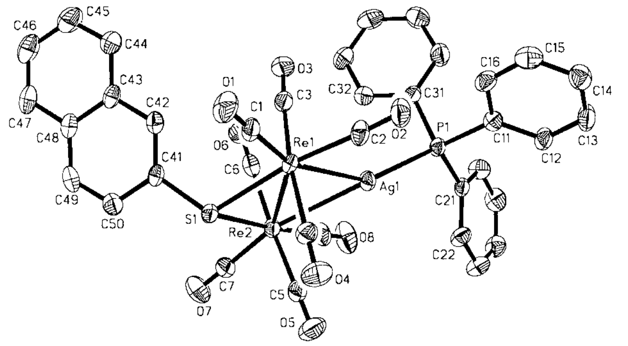


Fig. 3 Molecular structure of complex **5b**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1077(8), Re1–S1 2.464(1), Re2–S1 2.473(1), Re1–Ag1 2.8199(9), Re2–Ag1 2.8476(6), S1–C41 1.787(5) and Ag1–P1 2.448(1); Re1–S1–Re2 78.01(4), Re1–Ag1–Re2 66.50(2), S1–Re1–Re2 51.12(3), S1–Re2–Re1 50.86(3), Ag1–Re1–Re2 57.17(1), Ag1–Re2–Re1 56.32(1), P1–Ag1–Re1 147.14(4) and P1–Ag1–Re2 138.05(4).

Table 2 Crystallographic data for compounds **2c**, **2g**, **5a** and **5b**

Compound	**2c**	**2g**	**5a**	**5b**
Formula	$C_{14}H_{12}O_8Re_2S$	$C_{18}H_8O_8Re_2S$	$C_{36}H_{22}AuO_8PRe_2S$	$C_{36}H_{22}AgO_8PRe_2S$
M	712.7	756.7	1214.9	1125.8
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
T/K	293(2)	210(2)	293(2)	203(2)
a/Å	10.399(2)	7.047(3)	11.518(1)	11.380(2)
b/Å	11.555(3)	16.792(4)	12.435(3)	12.439(2)
c/Å	16.244(5)	16.853(4)	14.839(1)	14.722(2)
α/°			85.64(1)	76.80(2)
β/°	98.63(2)	91.23(2)	68.17(1)	67.37(2)
γ/°			64.39(1)	64.24(2)
U/Å^3	1929.8(9)	1993.8(11)	1770.1(5)	1727.7(6)
Z	4	4	2	2
μ(Mo-Kα)/mm^{-1}	12.67	12.28	11.11	7.71
Reflections (measured/unique)	4567/4434	4746/4599	9248/8053	9098/7909
R_{int}	0.057	0.034	0.022	0.019
$R1/wR2$	0.047/0.111	0.045/0.127	0.055/0.145	0.031/0.066

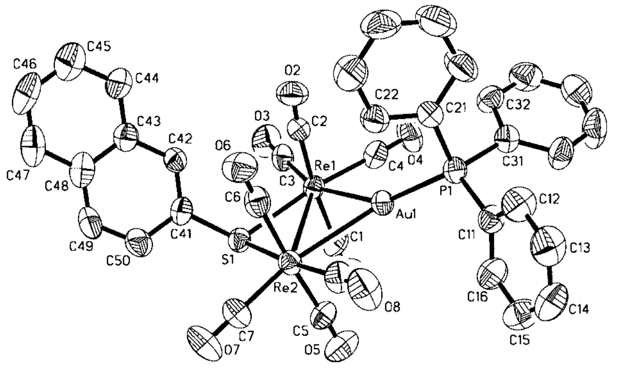


Fig. 4 Molecular structure of complex **5a**. Hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): Re1–Re2 3.1356(7), Re1–S1 2.469(2), Re2–S1 2.465(2), Re1–Au1 2.7853(8), Re2–Au1 2.8110(7), S1–C41 1.769(9) and Au1–P1 2.324(2); Re1–S1–Re2 78.91(7), Re1–Au1–Re2 68.15(2), S1–Re1–Re2 50.49(6), S1–Re2–Re1 50.59(6), Au1–Re1–Re2 56.31(1), Au1–Re2–Re1 55.54(1), P1–Au1–Re1 148.14(6) and P1–Au1–Re2 139.18(6).

corresponding molecular structures with μ-PR_2 instead of the μ-S(2-naph) group.[15,18]

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. The PLC 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 HSR (R = 2-naphthyl, Ph, *n*-Bu, Cy or C_6H_4-F-*p*), dbu and PPh_4Cl were purchased from Fluka, $[Re_2(CO)_{10}]$ from Acros and HSC_6F_5 from Aldrich. All reagents were laboratory grade and used as received. The complexes $[Re_2(CO)_8(MeCN)_2]$,[19] $[AuCl(PPh_3)]$,[20] $[AgCl(PPh_3)]$[21] and $[CuCl(PPh_3)]$[22] were prepared according to literature methods.

Preparations

Re$_2$(μ-H)(μ-SR)(CO)$_8$ 2. The complex $[Re_2(CO)_8(MeCN)_2]$ **1** (120 mg, 0.177 mmol) and 2 equivalents (0.354 mmol) of HSR were dissolved in 20 ml of toluene. In the case of R = H a gentle stream of H_2S was passed for 30 s through a solution of **1** in toluene. Subsequently the reaction mixture was heated to 80 °C. All the starting material reacts within 13 to 30 min as shown by the disappearance of the characteristic IR absorption of **1** at 2069 cm^{-1}. The reaction times are dependent on the thiol used. The solution was cooled to room temperature and after solvent removal the crude material was purified by PLC using the following solvent mixtures: R = H, CH_2Cl_2–*n*-hexane (1 : 7); R≠H, CH_2Cl_2–*n*-hexane (1 : 5). The colourless products [Re$_2$(μ-H)(μ-SR)(CO)$_8$] (R = H **2a**, *n*-Bu **2b**, Cy **2c**, Ph **2d**, C_6H_4F-*p* **2e**, C_6F_5 **2f** or 2-naphthyl **2g**) were obtained in the following yields (mg, %): 71, 64; 92, 76; 101, 80; 79, 63; 77, 60; 90, 64; and 96, 72 (Found: C, 15.11; H 0.23. $C_8H_2O_8Re_2S$ **2a** requires C, 15.24; H, 0.32. Found: C, 21.14; H, 1.54. $C_{12}H_{10}O_8Re_2S$ **2b** requires C, 20.99; H, 1.47. Found: C, 23.29; H, 1.58. $C_{14}H_{12}O_8Re_2S$ **2c** requires C, 23.60; H, 1.70. Found: C, 23.30; H, 0.98. $C_{14}H_6O_8Re_2S$ **2d** requires C, 23.80; H, 0.86. Found: C, 23.34; H, 0.66. $C_{14}H_5FO_8Re_2S$ **2e** requires C, 23.20; H, 0.70. Found: C, 21.15; H, 0.21. $C_{14}HF_5O_8Re_2S$ **2f** requires C, 21.11; H, 0.13. Found: C, 28.47; H, 1.19. $C_{18}H_8O_8Re_2S$ **2g** requires C, 28.57; H, 1.07%).

[{Re$_2$(μ-H)(CO)$_8$}$_2$(μ$_4$-S)] 3. Complexes **2a** (70 mg, 0.111 mmol) and **1** (110 mg, 0.162 mmol) were dissolved in 20 ml toluene. The mixture was heated to 80 °C until **1** was no longer detectable by IR spectroscopy. Upon cooling a colourless precipitate formed. The solution was concentrated *in vacuo* to 5 ml and subsequently cooled to 5 °C for 24 h in order to complete the formation of the precipitate. Then the cold solution was decanted from the precipitate. The latter was washed five times with CH_2Cl_2–*n*-hexane (1 : 1) to give pure **3** in 54% yield (74 mg) (Found: C, 15.39; H, 0.25. $C_{16}H_2O_{16}Re_4S$ requires C, 15.66; H, 0.16%).

[PPh$_4$][Re$_2$(μ-S(2-naph))(CO)$_8$] 4. To a colourless solution of 150 mg (0.198 mmol) [Re$_2$(μ-H)(μ-S(2-naph))(CO)$_8$] **2g** in 5 ml thf were added 74 μl (0.495 mmol) dbu. The mixture turned yellow within 30 min. After 4 h the deprotonation is complete as evidenced by IR measurements. Subsequently 75 mg (0.2 mmol) PPh_4Cl were added and the solution stirred for five minutes. The solvent was removed under vacuum and the residue taken up in 10 ml of methanol. Upon slow addition of water a yellow precipitate formed. This was collected by filtration, washed three times with 5 ml water and 5 ml *n*-hexane, and finally dried in vacuum to give pure complex **4**. Yield: 184 mg, 85%. Found: C, 46.20; H, 2.33. $C_{42}H_{27}O_8PRe_2S$ requires C, 46.06; H, 2.49%).

[Re$_2$(MPPh$_3$)(μ-S(2-naph))(CO)$_8$] 5. Complex **4** (150 mg, 0.137 mmol) was dissolved in 10 ml chloroform. Upon addition of equimolar amounts of [MCl(PPh$_3$)] (M = Au, 68 mg; Ag, 56 mg; Cu, 49 mg) solution changed from pale to deep yellow. After 30 min the solvent was removed and the residue separated by PLC [eluent dichloromethane–*n*-hexane (1 : 1)]. The major yellow band gave [Re$_2$(MPPh$_3$)(μ-S(2-naph))(CO)$_8$] (M = Au **5a**, Ag **5b** or Cu **5c**) in the following yield (mg, %): 140, 87; 100, 65; 58, 39 (Found: C, 35.41; H, 1.81. $C_{36}H_{22}AuO_8PRe_2S$ **5a** requires C, 35.59; H, 1.83). (Found: C, 38.47; H, 2.10. $C_{36}H_{22}AgO_8PRe_2S$ **5b** requires C, 38.40; H, 1.97). (Found: C, 40.04; H, 1.93. $C_{36}H_{22}CuO_8PRe_2S$ **5c** requires C, 39.98; H, 2.05%).

Crystal structure determinations

Pertinent crystallographic data for compounds **2c**, **2g**, **5a** and **5b** 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 showed only random deviations. Intensities 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 anisotropically; geometrically placed hydrogen atoms were refined with a riding model. The μ-H atom of structure **2c** was determined from the ΔF map and refined, that of **2g** was not located and not included in the refinement. Programs used for calculations: SHELX 97.[23]

CCDC reference number 186/1594.

See http://www.rsc.org/suppdata/dt/1999/3203/ for crystallographic files in .cif format.

Acknowledgements

We thank Degussa for the generous loan of HAuCl$_4$·3H$_2$O.

References

1 H.-J. Haupt, P. Balsaa and U. Flörke, *Z. Anorg. Allg. Chem.*, 1987, **548**, 151; H.-J. Haupt, O. Krampe and U. Flörke, *Z. Anorg. Allg. Chem.*, 1996, **622**, 807.

2 J. Grobe and W. Mohr, *J. Fluorine Chem.*, 1976, **8**, 145; R. D. Adams and J. D. Kuhns, *Polyhedron*, 1988, **7**, 2543; G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi and M. Freni, *Inorg. Chem.*, 1983, **22**, 3115.

3 P. O. Nubel, S. R. Wilson and T. L. Brown, *Organometallics*, 1983, **2**, 515; D. R. Gard and T. L. Brown, *Organometallics*, 1982, **1**, 1143.

4 S. Top, M. Gunn, G. Jaoen, J. Vaissermann, J.-C. Daran and J. R. Thornback, *J. Organomet. Chem.*, 1991, **414**, C22.

5 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 1984, **106**, 644.

6 C. G. Kreiter, K.-H. Franzreb and W. S. Sheldrick, *J. Organomet. Chem.*, 1984, **270**, 71.

7 H.-J. Haupt, A. Merla and U. Flörke, *Z. Anorg. Allg. Chem.*, 1994, **620**, 999; H.-G. Beckers, U. Flörke and H.-J. Haupt, *Angew. Chem.*, 1995, **107**, 1464; H.-J. Haupt, U. Siefert and U. Flörke, *Z. Kristallogr.*, 1996, **211**, 695; H.-J. Haupt, M. Schwefer, H. Egold and U. Flörke, *Inorg. Chem.*, 1997, **36**, 184; H. Egold, M. Schraa and U. Flörke, *J. Organomet. Chem.*, 1999, **582**, 345.

8 R. Wittbecker, Ph.D. Thesis, University of Paderborn, 1997.

9 T. Beringhelli, G. D'Alfonso, G. Ciani, M. Moret and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1993, 1101; R. D. Adams, L. Chen and W. Wu, *Organometallics*, 1993, **12**, 4962.

10 G. A. Foulds, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1985, **296**, 147; R. D. Adams, T. Barnard, A. Rawlett and J. M. Tour, *Eur. J. Inorg. Chem.*, 1998, 429; P. Braunstein, J. R. Galsworthy, B. J. Hendan and H. C. Marsmann, *J. Organomet. Chem.*, 1998, **551**, 125; S.-M. Lee, K. K. Cheung and W.-T. Wong, *J. Cluster Sci.*, 1996, **7**, 435; E. W. Ainscough, A. M. Brodie, R. K. Coll, A. J. A. Mair and J. M. Waters, *J. Organomet. Chem.*, 1996, **509**, 259; M. Monari, R. Pfeiffer, U. Rudsander and E. Nordlander, *Inorg. Chim. Acta*, 1996, **247**, 131.

11 H. Egold, D. Schwarze and U. Flörke, unpublished results.

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

13 R. D. Adams, J. E. Cortopassi and S. B. Falloon, *Organometallics*, 1992, **11**, 3794.

14 H.-J. Haupt, C. Heinekamp and U. Flörke, *Z. Anorg. Allg. Chem.*, 1990, **585**, 168; A. Merla, U. Flörke and H.-J. Haupt, *Z. Anorg. Allg. Chem.*, 1994, **620**, 999.

15 H.-J. Haupt, C. Heinekamp and U. Flörke, *Inorg. Chem.*, 1990, **29**, 2955; C. Heinekamp, Ph.D. Thesis, University of Paderborn, 1990.

16 C. A. Dullaghan, G. B. Carpenter, D. A. Sweigart, D. S. Choi, S. S. Lee and Y. K. Chung, *Organometallics*, 1997, **16**, 5688.

17 U. Flörke and H.-J. Haupt, unpublished results.

18 H.-J. Haupt, M. Schwefer and U. Flörke, *Z. Anorg. Allg. Chem.*, 1995, **621**, 1098.

19 J. Powell, J. C. Brewer, G. Gulia and J. F. Sawyer, *J. Chem. Soc., Dalton Trans.*, 1992, 2503.

20 G. Brauer, *Handbuch der präparativen Anorganischen Chemie*, F. Enke Verlag, 3rd edn., vol. 3, 1981, p. 2019.

21 F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, 1965, **95**, 201.

22 F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, 1965, **95**, 3.

23 G. M. Sheldrick, SHELX 97, A program for Crystal Structure Solution and Refinement, University of Göttingen, 1998.

Paper 9/05111B