Formation of a μ_4-Methanedithiolate by Transfer of Two H Atoms from Re to a CS_2 Molecule. Synthesis and Crystal Structure of $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$†

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The reaction of the unsaturated dinuclear molecule $[Re_2(\mu\text{-}H)_2(CO)_8]$ with CS_2 affords in good yield the complex $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$, containing a methanedithiolate H_2CS_2 fragment originated by the transfer of two hydrides, presumably one from each metal complex, to CS_2. The molecule has been characterized spectroscopically and by single-crystal X-ray diffraction analysis. The crystals are monoclinic, space group $P2_1/c$, with $a = 13.559(1)$, $b = 12.502(1)$, $c = 16.718(1)$ Å, $\beta = 99.26(1)°$. The structure was refined on the basis of 2689 significant reflections to a final R value of 0.026. The molecule consists of two $Re_2(\mu\text{-}H)(CO)_8$ units linked by a methanedithiolate ligand. Each sulfur atom bridges two Re atoms belonging to the same dinuclear moiety. The overall idealized symmetry of the molecule is C_2. The average Re–Re and Re–S bond lengths are 3.089 and 2.475 Å, respectively.

We are currently investigating the hydrogen-transfer reactions from rhenium clusters to organic molecules containing polarized multiple bonds. In general, unsaturated hydridocarbonyl clusters are attractive starting materials, owing to the possibility of bonding to the same metallic framework both the substrate and the hydrogen transferred. Using the unsaturated anion $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$,[1] hydrogen transfer has been achieved to acetone[2a] and isonitriles,[2b,c] as well as to co-ordinated formyl[2d] or acyl[2e] groups. In this anion the unsaturation is located on the $Re(\mu\text{-}H)_2Re$ moiety, which is also present in some neutral dinuclear rhenium species, such as $[Re_2(\mu\text{-}H)_2(CO)_8]$[3] and $[Re_2(\mu\text{-}H)_2(CO)_6(Ph_2PCH_2PPh_2)]$.[4] The latter complex allowed hydrogen transfer to isonitriles and nitriles,[4] while no similar example has been reported for the former, likely because it seems prone to fragment upon reaction with donor molecules.[5] We have now found that $[Re_2(\mu\text{-}H)_2(CO)_8]$ is able to transfer hydrogen to a CS_2 molecule, giving a H_2CS_2 methanedithiolate fragment, co-ordinated through sulfur bridges to four rhenium atoms.

Results and Discussion

When $[Re_2(\mu\text{-}H)_2(CO)_8]$ is dissolved in CS_2, distilled directly into the reaction vessel, a slow reaction occurs, as evidenced by progressive darkening of the yellow solution and by some small changes in the IR spectrum. At 45 °C the reaction goes to completion in about 6 h and ^1H NMR spectroscopy reveals the formation of a novel compound, exhibiting two resonances at δ 4.09 and -13.87 (in CS_2 containing a small amount of $[^2H_8]$toluene), with intensity ratio 1 : 1.

It is well known that CS_2 is able to insert into M–H bonds, with formation of co-ordinated dithioformate S_2CH groups.[6] In this case the observed 1 : 1 ratio between the hydridic and the 'organic' resonances in the NMR spectrum would be in agreement with this hypothesis. However, the chemical shift of the 'organic' resonance is much lower than expected for dithioformate ligands (usually $\delta \geqslant 10$).[6] Moreover, the IR absorptions characteristic of these groups[6] could not be detected. A single-crystal X-ray investigation allowed the novel compound to be formulated as $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$, containing two $Re_2(\mu\text{-}H)(CO)_8$ moieties bound by a H_2CS_2 group, as shown in Fig. 1.

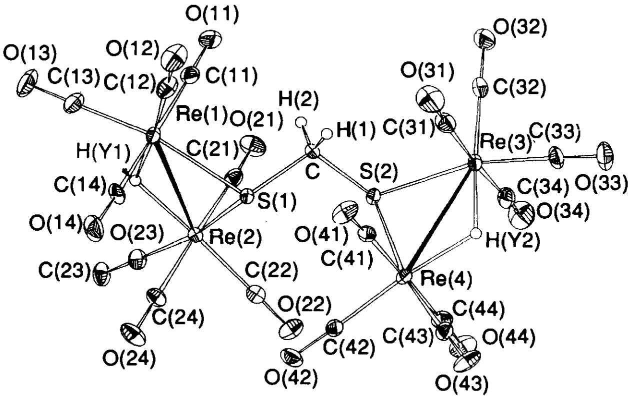

Fig. 1 A view of the $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$ molecule, with partial atom labelling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been given arbitrary radii

Few examples have been previously reported[7–9] of double hydride transfer to the carbon atom of CS_2, and these fall into two different classes according to the nature of the starting hydride complex. In the case of the mononuclear complexes $[Rh(\eta\text{-}C_5Me_5)(PMe_3)H_2]$[7] and $[Mo(\eta\text{-}C_5H_5)H_2]$[8], 1 mol of complex reduces 1 mol of CS_2 and the methanedithiolate moiety produced co-ordinates through the two S atoms, acting as a two-electron donor ligand, to give a tetrametallocycle. The rate-determining intermediate formation of a dithioformate ligand was demonstrated for the rhodium complex.[7] On the contrary, in the case of the unsaturated triangular clusters $[Os_3(\mu\text{-}H)_2(CO)_9L]$ (L = CO or PMe_2Ph),[9] 2 mol of the complexes react with 1 mol of CS_2, leading to derivatives $[\{Os_3(\mu\text{-}H)(CO)_9L\}_2(\mu_4\text{-}S_2CH_2)]$, in which, as in $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$, each S atom of the methanedithiolate

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Relevant bond distances (Å) and angles (°) for $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$ with estimated standard deviations (e.s.d.s) in the least significant digit in parentheses

Re(1)–Re(2)	3.093(1)	Re(2)–C(21)	1.97(1)	Re(4)–C(43)	1.95(1)	O(23)–C(23)	1.12(1)
Re(3)–Re(4)	3.085(1)	Re(2)–C(22)	1.94(1)	Re(4)–C(44)	1.99(1)	O(24)–C(24)	1.14(1)
Re(1)–S(1)	2.475(3)	Re(2)–C(23)	1.96(1)	S(1)–C	1.81(1)	O(31)–C(31)	1.12(2)
Re(2)–S(1)	2.473(3)	Re(2)–C(24)	1.99(1)	S(2)–C	1.83(1)	O(32)–C(32)	1.17(1)
Re(3)–S(2)	2.482(3)	Re(3)–C(31)	1.98(2)	O(11)–C(11)	1.14(1)	O(33)–C(33)	1.14(1)
Re(4)–S(2)	2.469(3)	Re(3)–C(32)	1.91(2)	O(12)–C(12)	1.16(2)	O(34)–C(34)	1.14(2)
Re(1)–C(11)	1.98(2)	Re(3)–C(33)	1.93(1)	O(13)–C(13)	1.14(1)	O(41)–C(41)	1.12(1)
Re(1)–C(12)	1.91(1)	Re(3)–C(34)	1.99(1)	O(14)–C(14)	1.13(1)	O(42)–C(42)	1.16(1)
Re(1)–C(13)	1.92(1)	Re(4)–C(41)	1.98(1)	O(21)–C(21)	1.14(1)	O(43)–C(43)	1.12(1)
Re(1)–C(14)	1.97(1)	Re(4)–C(42)	1.92(1)	O(22)–C(22)	1.14(1)	O(44)–C(44)	1.13(1)
Re(2)–Re(1)–S(1)	51.27(7)	Re(4)–Re(3)–S(2)	51.28(7)	S(1)–Re(2)–C(22)	99.1(4)	S(2)–Re(4)–C(42)	99.6(4)
S(1)–Re(1)–C(11)	94.5(4)	S(2)–Re(3)–C(31)	96.1(5)	S(1)–Re(2)–C(23)	166.3(4)	S(2)–Re(4)–C(43)	168.1(4)
S(1)–Re(1)–C(12)	98.8(4)	S(2)–Re(3)–C(32)	101.2(4)	S(1)–Re(2)–C(24)	88.4(4)	S(2)–Re(4)–C(44)	88.5(4)
S(1)–Re(1)–C(13)	167.1(4)	S(2)–Re(3)–C(33)	165.6(4)	C(21)–Re(2)–C(22)	88.1(5)	C(41)–Re(4)–C(42)	90.4(5)
S(1)–Re(1)–C(14)	85.9(4)	S(2)–Re(3)–C(34)	85.4(4)	C(21)–Re(2)–C(23)	91.0(6)	C(41)–Re(4)–C(43)	89.2(5)
C(11)–Re(1)–C(12)	90.5(6)	C(31)–Re(3)–C(32)	87.6(6)	C(21)–Re(2)–C(24)	176.0(5)	C(41)–Re(4)–C(44)	179.4(5)
C(11)–Re(1)–C(13)	89.9(6)	C(31)–Re(3)–C(33)	88.6(7)	C(22)–Re(2)–C(23)	93.4(6)	C(42)–Re(4)–C(43)	92.3(5)
C(11)–Re(1)–C(14)	178.8(6)	C(31)–Re(3)–C(34)	175.7(6)	C(22)–Re(2)–C(24)	89.6(5)	C(42)–Re(4)–C(44)	89.4(6)
C(12)–Re(1)–C(13)	93.2(6)	C(32)–Re(3)–C(33)	92.6(6)	C(23)–Re(2)–C(24)	85.9(5)	C(43)–Re(4)–C(44)	90.2(5)
C(12)–Re(1)–C(14)	88.3(6)	C(32)–Re(3)–C(34)	88.2(6)	Re(1)–S(1)–Re(2)	77.39(8)	Re(3)–S(2)–Re(4)	77.06(8)
C(13)–Re(1)–C(14)	90.0(6)	C(33)–Re(3)–C(34)	90.9(7)	Re(1)–S(1)–C	109.6(4)	Re(3)–S(2)–C	111.1(4)
Re(1)–Re(2)–S(1)	51.35(7)	Re(3)–Re(4)–S(2)	51.66(7)	Re(2)–S(1)–C	112.9(4)	Re(4)–S(2)–C	110.3(4)
S(1)–Re(2)–C(21)	95.1(4)	S(2)–Re(4)–C(41)	92.1(3)	S(1)–C–S(2)	110.8(6)	Re–C–O	175(1)–179(1)

Table 2 Summary of Re–Re bond lengths (Å) and valence electrons for $Re_2(CO)_8(\mu\text{-}X)(\mu\text{-}Y)$ and related compounds

Compound	d_{Re-Re}	Valence electrons	Bond order	Ref.
$[Re_2(\mu\text{-}H)_2(CO)_8]$	2.876(1)	32	2	3, 16
$[Re(CO)_8(\mu\text{-}PPh_2)(\mu\text{-}AuPPh_3)]$	3.225(2)	34	1	17
$[Re_2(CO)_8\{\mu\text{-}GaRe(CO)_5\}_2]$	3.139(2)	34	1	18
$[Re_2(CO)_8\{\mu\text{-}InRe(CO)_5\}_2]$	3.232(2)	34	1	19
$[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$	3.085(1) 3.093(1)	34	1	This work
$[Re_2(CO)_8(\mu\text{-}I)_2]$	4.218(2)	36	0	20
$[Re_2(CO)_8(\mu\text{-}PPh_2)_2]$	3.928(1)	36	0	21
$[Re_2(CO)_8\{\mu\text{-}SC(S)S[Re(CO)_4]\}_2]$	3.889(1)	36	0	22
Related compounds				
$[Re_2(CO)_8(\mu\text{-}PPh_2)]^-$	3.062(1)	34	1	17
$[Re_2(\mu\text{-}H)(CO)_7(PPh_3)(\mu\text{-}PPh_2)]$	3.152(1)	34	1	23
$[Re_2(\mu\text{-}H)(CO)_6(PPh_3)_2(\mu\text{-}PPh_2)]$	3.194(1)	34	1	24
$[Re_2(CO)_7(SbPh_3)(\mu\text{-}PPh_2)(\mu\text{-}SbPh_2)]$	4.150(1)	36	0	21

ligand donates three electrons to the cluster. The similarity between the reaction here reported and that of the triosmium cluster is not surprising, since in both cases the hydrides involved belong to $M(\mu\text{-}H)_2M$ units. It seems therefore reasonable that the formation of the present compound occurs through a mechanism analogous to that proposed for the osmium cluster, for which intermediate dithioformate complexes have been ruled out.[9] The first step, according to the typical chemical behaviour of these unsaturated species, would be the addition of 1 mol of CS_2, to give a 1 : 1 adduct, in which CS_2 should be η^2-co-ordinated, through C and one S atom. This co-ordination mode is known[10] to increase the nucleophilicity of the remaining sulfur atom, allowing it to interact with a second molecule of $[Re_2(\mu\text{-}H)_2(CO)_8]$. The double hydrogen transfer would then occur in the resulting 2 : 1 adduct.[9] The IR and NMR spectra of $[Re_2(\mu\text{-}H)_2(CO)_8]$ in CS_2 are quite similar to those observed in non-co-ordinating solvents, such as hexane, and therefore the *fast* formation of *detectable* amounts of adducts can be ruled out. Moreover, no intermediate could be detected by NMR monitoring of the reaction. These data indicate either a rate-determining adduct formation or a quite low equilibrium concentration of the adducts.

The Structure of $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$.—The crystal structure consists of the packing of discrete neutral molecules with normal intermolecular contacts, the shortest, between carbonyl C and O atoms, being larger than 3 Å. Relevant bond distances and angles are reported in Table 1.

The molecule of $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$, Fig. 1, is composed of two $Re_2(\mu\text{-}H)(CO)_8$ dinuclear units linked by a methanedithiolate ligand; each sulfur atom bridges two Re atoms belonging to the same dinuclear unit. The overall idealized symmetry of the molecule is C_2 with the two-fold axis bisecting the S(1)–C–S(2) angle. The dihedral angle between the two Re_2S triangles is 107.5°.

Several complexes containing $\mu\text{-}S_2CH_2$ ligands have been structurally characterized, most being obtained by routes different from CS_2 reduction. Among these, the most closely related to the present complex, both chemically and structurally, is the osmium compound $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu_4\text{-}S_2CH_2)]$.[9]

The Re atoms possess, neglecting the metal–metal interactions, a distorted-octahedral co-ordination sphere comprising four terminal CO, one sulfur atom and one hydride ligand. The hydrogen atoms were not directly identified by Fourier difference synthesis, but the presence of two bridging hydrides is supported by the stereochemistry of the other ligands, in line with the ^1H NMR spectrum. The positions of the hydrides were calculated by use of the program HYDEX.[11] These hydrides [H(Y1) and H(Y2)] are coplanar with the Re_2S planes, the out-of-plane displacements being about 0.05 and 0.09 Å, respectively.

Structural data are in full agreement with the presence of a methanedithiolate ligand, instead of a dithioformate one, owing to the C–S bond distances of 1.81(1) and 1.83(1) Å (average 1.85 Å in $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu_4\text{-}S_2CH_2)]$,[9] 1.820(5) Å in $[Fe_2(CO)_6(\mu\text{-}S_2CH_2)]$[12]), significantly longer than those usually found for dithioformate ligands (1.64–1.68 Å).[13] The S(1)–C–S(2) bond angle of 110.8(6)° indicates an almost perfect tetrahedral geometry at the methylene carbon atom. The average Re–S–C angles (111.0°) and the pyramidalization around the S atoms [S(1) 0.966(3) and S(2) 0.986(3) Å off the Re(1), Re(2), C and Re(3), Re(4), C planes, respectively] indicate an sp^3 hybridization of the sulfur atoms, the fourth co-ordination site being occupied by a lone pair.

The Re–S interactions range from 2.469(3) to 2.482(3) Å. For a comparison of these interactions the only related compounds are $[ClRe(\mu\text{-}S_2CMe_2)(\mu\text{-dppm})_2ReCl]$ (dppm = $Ph_2PCH_2PPh_2$)[14] containing a triply bonded metal core with a Re–Re bond length of 2.2544(6) Å and Re–S distances of 2.471(3) and 2.485(3) Å, and $[(OC)_4Re\{\mu\text{-}S_2CP(C_6H_{11})_3\}Re(CO)_4]$,[15] which exhibits mean Re–S and C–S bond distances of 2.452 and 1.678 Å, respectively, the latter value being typical of dithioformate ligands.

The average Re–Re distance (3.089 Å) is significantly longer than the analogous interaction in $[(OC)_4Re\{\mu\text{-}S_2CP(C_6H_{11})_3\}Re(CO)_4]$ [2.987(1) Å] where the only bridging ligand is a dithiocarboxylate group. The significant lengthening can be ascribed to the hydride ligands the presence of which is normally associated with a stretching of the metal–metal bonds.

The compound $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$ represents the first example of a structurally characterized $Re_2(CO)_8(\mu\text{-}H)(\mu\text{-}X)$ complex. For the purpose of comparison in Table 2 are collected all the structurally characterized compounds of general formula $Re_2(CO)_8(\mu\text{-}X)(\mu\text{-}Y)$. The different complexes are classified according to the number of valence electrons and the formal bond order for the Re–Re interaction. The Re–Re distance strongly depends on the bond order and ranges from 2.876 Å for $[Re_2(\mu\text{-}H)_2(CO)_8]$ with 32 valence electrons, bond order 2, to values of more than 4 Å for the non-bonding interactions within the compounds having 36 valence electrons and bond order 0.

The CO ligands are all linear within experimental error (Re–C–O angles in the range 175–179°). The Re–C bond lengths fall in three distinct categories: eight CO *trans* to another CO (mean Re–C 1.98 Å), four CO *trans* to a Re–S interaction (mean Re–C 1.94 Å) and four CO *trans* to a hydride (mean Re–C 1.92 Å); this structural *trans* influence reflects the decreased competition in the same order for the electron density from the metal.

Experimental

Carbon disulfide (Merck) was distilled over P_2O_5 under N_2 directly into the reaction vessel. The complex $[Re_2(\mu\text{-}H)_2(CO)_8]$ was prepared by published methods.[5] The IR spectra were recorded in 0.1 mm CaF_2 cells on a Perkin-Elmer 781 grating spectrophotometer, equipped with a data station using PE780 software, NMR spectra on a Bruker WP80 spectrometer and mass spectra on a VG 7070EQ instrument. Elemental analyses were performed by the Microanalytical Laboratory of our Department.

Synthesis of $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$.—Carbon disulfide (6 cm^3) was distilled under N_2 into a Schlenk tube containing solid $[Re_2(\mu\text{-}H)_2(CO)_8]$ (65 mg, 0.109 mmol). The tube was immersed in an oil-bath at 45 °C for 6 h, then the solvent was removed under reduced pressure. Infrared and NMR analysis of the orange-brown residue showed only the signals of $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$: IR ($\nu_{CO}$, CH_2Cl_2) 2106w, 2095m, 2022vs, 2010 (sh) and 1968 (br) cm^{-1} (*cf.* 2096m, 2023vs, 2000ms and 1971s cm^{-1} for the starting compound, in the same solvent); ^1H NMR ([$^2H_6$]acetone), δ 4.30 (s, 1) and −13.83 (s, 1). The compound could be purified by column chromatography [SiO_2, CH_2Cl_2–hexane (2:1), nitrogen atmosphere], but with some loss due to decomposition (31 mg, 0.024 mmol, isolated yields 45%) (Found: C, 16.20; H, 0.40. $C_{17}H_4O_{16}Re_4S_2$ requires C, 16.00; H, 0.30%). The electron-impact mass spectrum was the superimposition of the spectra of $[Re_3(\mu\text{-}H)_3(CO)_{12}]$ (main species)[25a] and $[Re_2(CO)_{10}]$,[25b] indicating complete decomposition of the compound under the mass spectrometer conditions [200 °C, 10^{-7} Torr (*ca.* 1.33 × 10^{-5} Pa)].

Crystal Structure Determination of $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$.—*Intensity measurements.* A yellow crystal of dimensions 0.20 × 0.07 × 0.06 mm was mounted on a glass fibre in the air. Data were measured on an Enraf-Nonius CAD4 automatic diffractometer using graphite-monochromated Mo-Kα radiation. The setting angles of 25 intense reflections having 2θ in the range 16–22° were used in a least-squares refinement to determine accurately the unit-cell parameters and an orientation matrix relating the crystal axes to the diffractometer axes. Intensity data were collected at room temperature by the ω-scan method with variable scan speed (maximum scan time for each reflection 70 s) and variable scan range (0.9 + 0.35 tan θ) with a 25% extension at each end of the scan range for background determination. A total of 5150 diffracted intensities were measured by exploring the octants of the reciprocal lattice with $-16 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 14$ and $0 \leqslant l \leqslant 19$ out to a maximum 2θ angle of 50°. Three standard reflections were monitored every 3 h; the observed crystal decay was accounted for by applying drift corrections between 0.99 and 1.04. The diffracted intensities were also corrected for Lorentz, polarization and background effects. An empirical absorption correction was applied to the data set based on ψ scans[26] (ψ 0–360°, every 10°) of three suitable reflections with χ values close to 90°; relative transmission factors 1.00–0.77.

Structure solution and refinements. All the calculations were performed on a PDP11/73 computer using the SDP Plus

Table 3 Summary of crystal data and data collection/analysis parameters for $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$

Formula	$C_{17}H_4O_{16}Re_4S_2$
M	1273.14
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	13.559(1)
b/Å	12.502(1)
c/Å	16.718(1)
β/°	99.26(1)
U/Å^3	2797.0(7)
Z	4
D_c/g cm^{-3}	3.021
$F(000)$	2264
μ(Mo-Kα)/cm^{-1}	176.95
Minimum relative transmission factor	0.77
θ range/°	3–25
Required $\sigma(I)/I$	0.01
Octants of reciprocal space collected	$\pm h, \pm k, \pm l$
Crystal decay (%)	4
No. collected reflections (at room temperature)	5150
No. unique observed reflections [$I > 3\sigma(I)$]	2689
No. of refined parameters	352
Max shift/error	< 0.01
R[a]	0.026
R'[b]	0.025
Goodness of fit[c]	1.052

[a] $R = \Sigma(|F_o - k|F_c||)/\Sigma F_o$. [b] $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o{}^2]$. [c] Goodness of fit = $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]$ where N_o and N_v are the number of observations and refined parameters, respectively.

Table 4 Fractional atomic coordinates for $[\{Re_2(\mu\text{-}H)(CO)_8\}_2(\mu_4\text{-}S_2CH_2)]$ with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	0.181 62(4)	0.126 00(4)	0.173 82(3)	O(44)	0.269 3(7)	−0.300 0(9)	0.573 8(5)
Re(2)	0.094 92(4)	0.070 69(4)	0.328 96(3)	C(11)	0.104 4(9)	0.009(1)	0.113 4(7)
Re(3)	0.343 00(4)	−0.381 45(4)	0.333 75(3)	C(12)	0.284(1)	0.111(1)	0.108 6(8)
Re(4)	0.387 28(4)	−0.190 25(4)	0.450 64(3)	C(13)	0.109(1)	0.229(1)	0.101 8(7)
S(1)	0.253 9(2)	0.011 1(2)	0.289 0(2)	C(14)	0.261(1)	0.242 6(9)	0.232 3(8)
S(2)	0.242 6(2)	−0.217 0(2)	0.342 3(2)	C(21)	0.015 0(9)	−0.048(1)	0.274 6(7)
C	0.250 9(9)	−0.127(1)	0.256 8(7)	C(22)	0.102 1(9)	−0.008(1)	0.430 0(7)
O(11)	0.058 7(7)	−0.057 1(8)	0.078 0(5)	C(23)	−0.026 3(9)	0.147(1)	0.344 5(8)
O(12)	0.347 2(7)	0.105(1)	0.069 7(6)	C(24)	0.169 1(9)	0.191(1)	0.389 3(7)
O(13)	0.064 3(8)	0.289 1(9)	0.059 0(6)	C(31)	0.432(1)	−0.320(1)	0.262 0(8)
O(14)	0.301 2(9)	0.312 3(8)	0.266 0(7)	C(32)	0.270(1)	−0.449(1)	0.239 7(8)
O(21)	−0.034 3(7)	−0.113 0(8)	0.242 2(6)	C(33)	0.434(1)	−0.500(1)	0.354 9(8)
O(22)	0.107 8(7)	−0.052 7(8)	0.489 7(5)	C(34)	0.250(1)	−0.450(1)	0.398 7(8)
O(23)	−0.092 7(6)	0.196 1(7)	0.353 2(5)	C(41)	0.465 4(8)	−0.119(1)	0.375 3(7)
O(24)	0.205 7(8)	0.260 6(8)	0.426 2(6)	C(42)	0.352 5(9)	−0.054(1)	0.490 9(7)
O(31)	0.482 6(9)	−0.289(1)	0.221 4(6)	C(43)	0.508 7(9)	−0.199(1)	0.530 8(7)
O(32)	0.228 8(8)	−0.491 6(9)	0.181 5(6)	C(44)	0.310 2(9)	−0.262(1)	0.527 2(7)
O(33)	0.489 6(8)	−0.569 2(8)	0.369 4(7)	H(Y1)	0.079 3	0.147 4	0.233 2
O(34)	0.191 4(8)	−0.487 4(9)	0.431 4(7)	H(Y2)	0.426 2	−0.324 8	0.422 1
O(41)	0.511 4(7)	−0.075 8(8)	0.335 1(5)	H(1)	0.310 1	−0.142 8	0.235 4
O(42)	0.331 3(7)	0.028 8(7)	0.514 0(5)	H(2)	0.194 3	−0.138 1	0.216 0
O(43)	0.579 7(6)	−0.203 5(9)	0.575 9(5)				

Structure Determination Package[27] and the physical constants tabulated therein. Scattering factors for neutral atoms and anomalous dispersion corrections for scattering factors were taken from refs. 28 and 29, respectively.

The structure was solved by three-dimensional Patterson and Fourier difference methods which gave all the non-hydrogen atom positions, and refined by full-matrix least squares using 2689 independent reflections with $I > 3\sigma(I)$, and minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Weights were assigned to individual observations following the expression $4F_o^2/\sigma^2(F_o^2)$, where $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/L_p$, $\sigma(I)$ is the standard deviation for each reflection as derived from counting statistics, p (optimized to 0.025) is a coefficient for improving the goodness of fit and L_p is the Lorentz-polarization factor. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogens could not be located in the Fourier difference maps. The methylene hydrogen atoms were placed in idealized positions with an sp^3 geometry for the carbon atom and d_{C-H} 0.95 Å, while the positions of the hydride ligands were calculated according to Orpen's program[11] with mean d_{Re-H} 1.85 Å. The hydrogen atoms were given isotropic B values of 5.0 Å^2 and their contribution to the structure factors was taken into account. The final values of the agreement indices R and R' were 0.026 and 0.025, respectively. The maximum residual in the final Fourier difference synthesis was 0.92 e Å^{-3}. Table 3 gives the crystal data and data collection parameters while the final atomic coordinates are collected in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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