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Photochemical reaction of $Re_2(CO)_{10}$ with tetramethylthiourea; structural characterization of two novel pentarhenium carbonyl complexes containing sulfido and tetramethyldiaminocarbene ligands, $[Re_5(CO)_{17}(\mu\text{-}R)(\mu_4\text{-}S)_2\{C(NMe_2)_2\}_2]$ (R = SH or OH)

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Abstract

Photochemical reaction of $[Re_2(CO)_{10}]$ with tetramethylthiourea $[S{=}C\{(NMe_2)_2\}]$ has led to the cleavage of the S=C bond yielding two novel rhenium carbonyl compounds $[Re_5(CO)_{17}(\mu\text{-}R)(\mu_4\text{-}S)\{C(NMe_2)_2\}_2]$ (R = SH **8** or OH **9**). The complexes have been characterised by spectroscopic methods and X-ray crystallography. The structure of **8** is based on a distorted Re_3S_3 octahedral cluster with meridonal arrangement of the three Re and three S atoms. Two of the S atoms are each bound to three Re atoms at the centre and also bonded to a terminally placed $Re(CO)_4\{C(NMe_2)_2\}$ moiety; the third S atom belongs to a SH group and bridges a pair of the meridonal Re atoms. Only two of the meridonal Re atoms lie within Re–Re bonding distance indicating that Re–Re bonds in $[Re_2(CO)_{10}]$ have also been cleaved during the reactions. Compound **9** is isostructural with **8**, with the OH group replacing the SH group. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Rhenium; Tetramethyldiaminocarbene; Carbonyl; Sulfido; Crystal structure

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1. Introduction

Reactions of thioureas with mono-, di- and poly-nuclear metal carbonyl complexes have been widely studied [1–21]. It has been observed that in polynuclear metal carbonyl complexes, the reaction conditions and the nature of the thiourea substituent have remarkable influence on the nature of products that are formed by a variety of bond rearrangements including cleavage of C–S, C–N, N–H and/or C–H bonds in alkyl substituted derivatives [11–21]. For example, bimetallic clusters of osmium $[(\mu\text{-}H)Os_3(CO)_9\{\mu_3\text{-}NRC(S)NHR\}]$ (R = H, **1** [19]; R = Ph, **2** [18]) and ruthenium $[(\mu\text{-}H)Ru_3(CO)_9\{\mu_3\text{-}NRC(S)NHR\}]$ (R = H, Me, Ph, **3** [11]) containing triply bridging thioureato ligands are formed by the cleavage of N–H bonds and coordination of both the sulfur and nitrogen atoms. *S*-coordinated tetramethylthiourea derivatives of $[Os_3(CO)_{12}]$, such as $[Os_3(CO)_{11}\{\eta'\text{-}SC(NMe_2)_2\}]$ and $[Os_3(CO)_9(\mu\text{-}$

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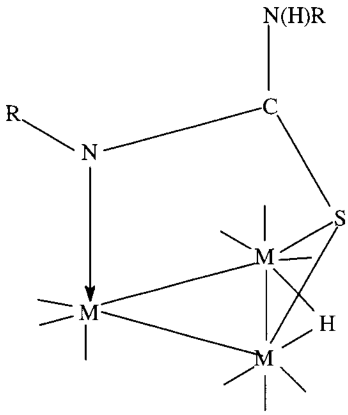
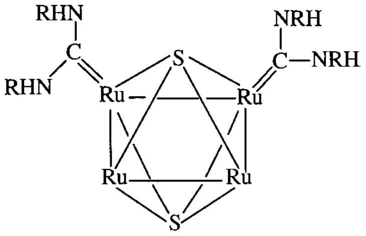
OH)(μ-OMeOCO){η^1-SC(NMe_2)$_2$}] have also been reported [19].



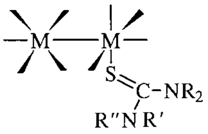
1. M = Os, R = H
2. M = Os, R = Ph
3. M = Ru, R = H, Me or Ph

The formation of ruthenium clusters [$Ru_4(CO)_6(\mu$-$CO)_3(\mu_4$-$S)_2${C(NHR)$_2$}$_2$] (R = Et, **4**; R = ^{i}Pr, **5**) containing sulfido and diaminocarbene ligands have been reported by the cleavage of the C=S bonds upon using more forcing conditions [14].



4, R = Et
5, R = ^{i}Pr

We have recently demonstrated that [$Mn_2(CO)_{10}$] undergoes photosubstitution while irradiated with a 125 W medium pressure mercury lamp to give the simple substitution product *eq*-[$Mn_2(CO)_9${η^1-SC(NMe_2)$_2$}] **6** [20]. Adams et al. reported the corresponding rhenium analog of *N*,*N*-diethyl-*N′*-*p*-tolylthiourea [$Re_2(CO)_9${η^1-SC(NEt_2)N(H)(*p*-tolyl)}] **7** from the labile monoacetonitrile compound [$Re_2(CO)_9$(MeCN)] [21].



6, M = Mn, R = R ′ = R″ = Me
7, M = Re, R ′ = Et, R ″ = p-tolyl, R = H

As a part of our continuing investigations of the chemistry of thiourea ligands, we have studied the photochemical reaction of [$Re_2(CO)_{10}$] with tetramethylthiourea using a 400 W high pressure mercury lamp. This has led us to the synthesis of two novel rhenium compounds which have been structurally characterized by X-ray diffraction analyses. The results of these studies are described herein.

2. Experimental

All manipulations were carried out either under vacuum or under a purified nitrogen atmosphere. Solvents were dried by standard methods and distilled prior to use. All reagents used were commercially available and were used without further purification. Photochemical reaction was performed with a RQ 400 W high pressure mercury lamp purchased from Applied Photophysics, UK. IR spectra were recorded on a Bruker IFS25 instrument. ^{1}H-NMR spectra were recorded on a Bruker AC200 spectrometer. Elemental analyses were carried out at the Microanalytical Laboratory, Institüt für Anorganische und Analytische Chemie, Universität Freiburg.

2.1. Photochemical reaction of [$Re_2(CO)_{10}$] with tetramethylthiourea

[$Re_2(CO)_{10}$] (0.200 g, 0.307 mmol) and tetramethylthiourea (0.405 g, 0.306 mmol) were dissolved in benzene (50 ml) and transferred to a Carius tube and degassed by freeze, pump, thaw cycles. The tube was then sealed under vacuum and irradiated with a 400 W high pressure mercury lamp for 4 h. The color of the reaction mixture changed from colorless to orange and a fine precipitate formed. The tube was allowed to cool to room temperature and opened carefully. The reaction mixture was separated from the precipitate by decantation. The solvent was removed by rotary evaporation and the residue was dissolved in a minimum volume of dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/CH_2Cl_2 (3:1, v/v) gave three bands. The faster-moving band gave unreacted starting material, [$Re_2(CO)_{10}$] (0.015 g). The second band gave [$Re_5(CO)_{17}(\mu$-SH$)(\mu_4$-$S)_2$]{C(NMe_2)$_2$}$_2$] **8** (0.073 g, 35%) obtained as yellow crystals after recrystallization from hexane/CH_2Cl_2 at − 20°C. Anal. Calc. for $C_{27}H_{25}N_4O_{17}Re_5S_3$: C, 19.02; H, 1.48; N, 3.29. Found: C, 19.32; H, 1.43; N, 3.21%. IR (νCO, CH_2Cl_2): 2098m, 2070w, 2060w, 2033m, 2014vs, 1989m, 1950sh, 1934s, 1910s, 1892sh cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.28 (s, 24H), 1.85 (s, 1H). The third band gave [$Re_5(CO)_{17}(\mu$-$OH)(\mu_4$-$S)_2$]{C(NMe_2)$_2$}$_2$] **9** (0.031 g, 15% as yellow crystals after recrystallization from hexane/CH_2Cl_2 at − 20°C. Anal. Calc. for $C_{27}H_{25}N_4O_{18}Re_5S_2$: C, 19.20; H, 1.49; N, 3.32. Found: C, 19.62; H,1.37; N, 3.30%. IR (νCO, CH_2Cl_2): 2097m, 2070w, 2059w, 2032m, 2011vs, 1990m, 1945w, 1928s, 1905s, 1885w cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.34 (s, 24H), − 1.25 (s, 1H).

2.2. X-ray crystallography

Crystals of the complexes **8** and **9** were obtained as described above. All measurements were made on a Delft Instruments FAST TV area detector diffractometer positioned at the window of rotating anode generator, using Mo–K_α radiation ($\lambda = 0.71069$ Å) in a manner described previously [22]. In both cases the unit cell parameters were obtained by least squares refinement of the diffractometer angles for 250 reflections. The crystallographic data, details of data collections and refinements are presented in Table 1. The data sets were corrected for Lorentz and polarisation factors, and also for absorption effects using DIFABS [23]. The structures were solved by direct methods (SHELXS86) [24] developed via difference syntheses, and refined on F^2 by full-matrix least- squares (SHELXL93) [25] using

Table 1
Crystal data and details of data collection and structure refinement[a] for $[Re_5(CO)_{17}(\mu_4\text{-}S)_2(\mu\text{-}SH)\{C(NMe_2)_2\}_2]$ **8** and $[Re_5(CO)_{17}(\mu_4\text{-}S)_2(\mu\text{-}OH)\{C(NMe_2)_2\}_2]$ **9**

	8	**9**
Chemical formula	$C_{27}H_{25}N_4O_{17}Re_5S_3$	$C_{27}H_{25}N_4O_{18}Re_5S_2$
Formula weight	1704.69	1688.63
Unit cell dimensions		
a (Å)	14.931(2)	14.934(3)
b (Å)	15.372(4)	15.444(3)
c (Å)	18.198(4)	17.938(4)
V (Å^3)	4177(2)	4137(2)
$D_{calc.}$ (g cm^{-3})	2.711	2.711
μ(Mo–K_α) (cm^{-1})	146.57	147.49
$F(000)$	3096	3064
Crystal size (mm)	$0.16 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.11$
θ range for data collection (°)	1.76–25.09	1.77–25.09
Index ranges	$-17 \leq h \leq 15$ $-17 \leq k \leq 18$ $-21 \leq l \leq 15$	$-16 \leq h \leq 16$ $-16 \leq k \leq 16$ $-13 \leq l \leq 19$
Reflections collected	13913	17080
Independent reflections	6508 [$R_{int} = 0.0894$]	6349 [$R_{int} = 0.0636$)
Absorption correction factors	0.820–1.138	0.853–1.173
Data/parameters	6508/513	6349/513
Goodness-of-fit on F^2	1.015	1.013
Absolute structure parameter	−0.04(2)	−0.04(2)
Final R[b] indices (all data)	$R_1 = 0.0554$, $wR_2 = 0.1125$	$R_1 = 0.0422$, $wR_2 = 0.0873$
R indices [$F_o^2 > 2\sigma(F_o^2)$]	$R_1 = 0.0492$, $wR_2 = 0.1112$	$R_1 = 0.0376$, $wR_2 = 0.0865$
Largest diff. peak and hole (e Å^{-3})	3.404 and −1.205	2.707 and −0.972

[a] Details in common: X-radiation, Mo–K_α, $\lambda = 0.71069$ Å, $T = 293$ K, orthorhombic, space group $P2_12_12_1$, $Z = 4$, refinement method: full-matrix least-squares on F^2 using all unique data.

[b] $R_1 = \Sigma[(F_o) - (F_c)]/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$; $w = [\sigma^2(F_o)^2 + (aP)^2]$, where $P = [(F_o)^2 + 2(F_c)^2]/3$, and $a = 0.0460$ (**8**) and 0.0409 (**9**).

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[Re_5(CO)_{17}(\mu_4\text{-}S)_2(\mu\text{-}SH)\{C(NMe_2)_2\}_2]$ **8**

	x	y	z	U(eq)
Re(1)	1996.4(5)	3806.1(5)	4618.1(4)	39(1)
Re(2)	1932.1(5)	4757.9(5)	3222.0(4)	37(1)
Re(3)	1512.2(5)	5887.5(5)	5106.7(4)	37(1)
Re(4)	4428.4(5)	5411.3(5)	4474.9(4)	40(1)
Re(5)	−851.2(5)	4423.9(5)	4160.1(5)	39(1)
S(1)	2746(3)	5223(3)	4337(2)	32(1)
S(2)	796(3)	4836(3)	4208(2)	32(1)
S(3)	1693(4)	4499(4)	5819(3)	59(2)
O(1)	2587(12)	2619(11)	3373(10)	81(5)
O(2)	3619(11)	2894(10)	5292(12)	83(6)
O(3)	775(11)	2287(12)	5006(11)	89(6)
O(4)	773(13)	3727(13)	2106(10)	81(6)
O(5)	3643(9)	4347(14)	2349(8)	77(6)
O(6)	1687(13)	6372(11)	2372(8)	80(6)
O(7)	−123(10)	6339(15)	6052(9)	90(7)
O(8)	2593(11)	6973(15)	6201(10)	93(7)
O(9)	1269(12)	7544(11)	4222(10)	77(5)
O(10)	6468(9)	5517(19)	4729(12)	128(10)
O(11)	4350(13)	7196(11)	5271(11)	89(6)
O(12)	4603(12)	3554(13)	3766(9)	77(5)
O(13)	4149(14)	4544(13)	6020(9)	90(6)
O(14)	−1626(11)	6144(12)	4862(12)	94(7)
O(15)	−637(15)	3703(16)	5757(11)	111(8)
O(16)	−129(13)	2689(12)	3488(10)	78(5)
O(17)	−2773(10)	3729(13)	4226(11)	88(6)
N(1)	−951(11)	5841(12)	2926(10)	54(5)
N(2)	−1287(16)	4478(17)	2485(12)	90(8)
N(3)	5336(15)	6036(14)	2999(11)	77(7)
N(4)	4060(15)	6750(14)	3167(10)	65(6)
C(1)	2330(15)	3149(16)	3769(12)	65(7)
C(2)	2998(13)	3234(15)	5045(12)	62(6)
C(3)	1243(13)	2862(14)	4884(14)	67(7)
C(4)	1214(13)	4113(14)	2519(13)	82(10)
C(5)	2983(12)	4470(17)	2669(10)	57(6)
C(6)	1754(12)	5728(11)	2695(9)	32(4)
C(7)	498(12)	6164(20)	5698(12)	80(8)
C(8)	2217(15)	6578(12)	5756(11)	54(6)
C(9)	1430(14)	6908(12)	4545(11)	47(5)
C(10)	5703(11)	5472(16)	4624(13)	65(6)
C(11)	4391(12)	6557(12)	4944(11)	46(5)
C(12)	4507(16)	4231(13)	4021(13)	63(7)
C(13)	4244(15)	4879(15)	5456(12)	62(6)
C(14)	−1303(15)	5515(14)	4635(14)	71(8)
C(15)	−727(19)	3987(19)	5177(14)	96(10)
C(16)	−425(17)	3310(14)	3745(13)	64(7)
C(17)	−2055(13)	4002(19)	4156(13)	83(9)
C(18)	−1022(13)	4994(13)	3036(11)	45(5)
C(19)	−405(13)	6433(12)	3371(13)	48(6)
C(20)	−1475(19)	6292(22)	2342(16)	106(12)
C(21)	−1759(23)	3668(19)	2487(15)	97(10)
C(22)	−1216(24)	4770(20)	1712(12)	110(13)
C(23)	4570(13)	6154(13)	3413(14)	51(6)
C(24)	5781(21)	5277(22)	2889(15)	106(12)
C(25)	5845(18)	6806(17)	2752(16)	82(9)
C(26)	3310(13)	7173(16)	3618(13)	65(7)
C(27)	3992(24)	7110(21)	2468(14)	108(12)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Re_5(CO)_{17}(\mu_4\text{-}S)_2(\mu\text{-}OH)\{C(NMe_2)_2\}_2]$ **9**

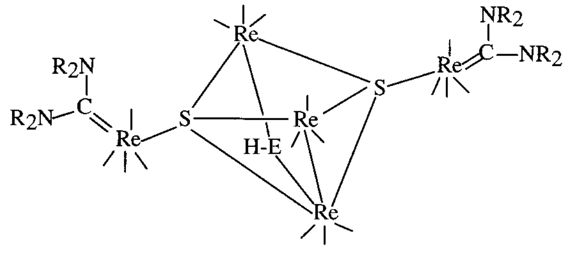
	x	*y*	*z*	*U*(eq)
Re(1)	1971.9(4)	3883.2(4)	4665.1(3)	43(1)
Re(2)	1890.0(4)	4804.7(4)	3200.6(3)	42(1)
Re(3)	1503.3(4)	5904.5(4)	5123.0(3)	40(1)
Re(4)	4402.0(4)	5451.6(4)	4449.4(3)	41(1)
Re(5)	−872.8(4)	4451.3(4)	4171.4(3)	44(1)
S(1)	2726(2)	5270(2)	4316(2)	36(1)
S(2)	764(2)	4882(2)	4204(2)	37(1)
O(1)	2521(10)	2655(9)	3399(8)	92(5)
O(2)	3570(9)	2900(9)	5330(8)	89(4)
O(3)	748(9)	2403(9)	5132(10)	98(5)
O(4)	760(9)	3710(10)	2109(7)	84(4)
O(5)	3596(8)	4455(13)	2280(7)	107(6)
O(6)	1614(12)	6458(9)	2312(7)	97(6)
O(7)	−112(10)	6330(12)	6112(7)	104(6)
O(8)	2593(10)	6973(10)	6236(8)	95(5)
O(9)	1237(9)	7560(9)	4249(7)	77(4)
O(10)	6434(8)	5534(16)	4722(10)	144(8)
O(11)	4300(10)	7277(8)	5234(8)	85(4)
O(12)	4538(9)	3566(8)	3752(8)	75(4)
O(13)	4068(10)	4649(10)	6007(7)	89(5)
O(14)	−1668(9)	6131(9)	4910(9)	98(5)
O(15)	−613(13)	3735(13)	5784(9)	125(7)
O(16)	−96(10)	2701(9)	3528(8)	84(4)
O(17)	−2817(9)	3748(10)	4218(10)	109(6)
O(18)	1718(7)	4631(7)	5636(5)	52(3)
N(1)	−963(9)	5828(10)	2895(7)	56(4)
N(2)	−1323(13)	4517(11)	2460(10)	87(6)
N(3)	5308(11)	6068(12)	2936(8)	81(6)
N(4)	3990(11)	6749(10)	3079(8)	69(4)
C(1)	2296(11)	3155(13)	3854(9)	69(6)
C(2)	2953(10)	3276(10)	5092(9)	56(4)
C(3)	1222(9)	2975(10)	4983(11)	68(6)
C(4)	1161(11)	4146(11)	2530(9)	58(5)
C(5)	2918(9)	4572(15)	2598(9)	77(6)
C(6)	1699(9)	5802(9)	2632(9)	53(4)
C(7)	504(10)	6187(12)	5723(9)	63(5)
C(8)	2193(11)	6557(11)	5809(8)	55(4)
C(9)	1364(11)	6907(9)	4567(8)	49(4)
C(10)	5660(9)	5503(15)	4610(11)	80(6)
C(11)	4355(10)	6619(9)	4919(8)	53(5)
C(12)	4510(12)	4266(10)	3984(9)	63(5)
C(13)	4166(11)	4961(11)	5424(8)	56(4)
C(14)	−1320(10)	5536(10)	4628(9)	52(4)
C(15)	−694(14)	4084(14)	5216(12)	96(8)
C(16)	−400(14)	3333(10)	3768(10)	64(6)
C(17)	−2089(11)	4009(14)	4174(13)	93(7)
C(18)	−1069(10)	5010(10)	3036(8)	40(4)
C(19)	−463(14)	6423(11)	3333(11)	75(6)
C(20)	−1527(14)	6280(17)	2332(11)	103(8)
C(21)	−1726(20)	3608(14)	2480(11)	106(9)
C(22)	−1195(22)	4795(17)	1685(12)	145(14)
C(23)	4543(12)	6151(11)	3347(9)	53(4)
C(24)	5829(15)	5280(15)	2892(11)	92(8)
C(25)	5799(15)	6844(15)	2688(11)	88(7)
C(26)	3296(12)	7181(11)	3518(10)	67(5)
C(27)	4042(16)	7071(17)	2365(11)	101(8)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

all unique data with intensities > 0. In all cases the non-hydrogen atoms were anisotropic; the methyl hydrogens were included in calculated positions (riding model) with $U_{iso} = 1.5 \times U_{eq}$ of the parent atoms, but those belonging to the SH (**8**) and OH (**9**) groups were ignored. The CO bond distances were restrained to refine to the same value within an e.s.d 0.01 Å. In both cases the determination of the correct absolute structure was indicated by the Flack parameter [26] 0.04(2) in SHELXL93. Final *R*-values are quoted in Table 1. The residual electron densities in the final difference maps did not indicate any feature of stereochemical significance. The atomic coordinates, and important bond lengths and angles are presented in Tables 2–5. Anisotropic displacement coefficients, hydrogen atom parameters and full lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. The calculations were performed on a Pentium 200 MHz personal computer. Sources of scattering factors as in [25]. Molecular diagrams were drawn with SNOOPI [27].

3. Results and discussion

The photochemical treatment of $[Re_2(CO)_{10}]$ with 1 equiv of tetramethylthiourea using a 400 W high pressure mercury lamp in benzene in a sealed tube resulted in two very interesting products. Instead of the expected dinuclear substitution product, we isolated two novel pentarhenium clusters containing sulfido and tetramethyldiaminocarbene ligands, $[Re_5(CO)_{17}(\mu\text{-}SH)(\mu_4\text{-}S)_2\{C(NMe_2)_2\}_2]$ **8** and $[Re_5(CO)_{17}(\mu\text{-}OH)(\mu_4\text{-}S)_2\{C(NMe_2)_2\}_2]$ **9** in 35 and 15% yields respectively. The composition and structures of these compounds were confirmed by elemental analysis, IR, ^{1}H-NMR and X-ray diffraction studies.



8, E = S, R = Me

9, E = O, R = Me

Clearly, the sulfido and diaminocarbene ligands originate from the cleavage of the C=S bonds of tetramethylthiourea ligand $SC(NMe_2)_2$. Similar behavior was observed when tetramethylthiourea was reacted with $[Ru_3(CO)_{12}]$ in refluxing THF to give the μ_4-S and diaminocarbene containing clusters $[Ru_4(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}S)_2\{C(NMe_2)_2\}]$ and $[Ru_4(\mu\text{-}CO)_2(CO)_7(\mu_4\text{-}S)_2\{C(NMe_2)_2\}_2]$ [13].

Table 4
Selected bond lengths (Å) and angles (°) for $[Re_5(CO)_{17}(\mu_4\text{-}S)_2(\mu\text{-}SH)\{C(NMe_2)_2\}_2]$ **8**

Re(1)–Re(2)	2.9334(12)	Re(1)–S(3)	2.474(6)
Re(1)–S(1)	2.502(5)	Re(1)–S(2)	2.505(4)
Re(2)–S(1)	2.471(4)	Re(2)–S(2)	2.471(4)
Re(3)–S(3)	2.512(6)	Re(3)–S(1)	2.530(4)
Re(3)–S(2)	2.536(5)	Re(4)–C(23)	2.26(2)
Re(4)–S(1)	2.541(4)	Re(5)–C(18)	2.24(2)
Re(5)–S(2)	2.542(4)		
Re–C(CO)	1.89[a]	Re–C(CO)	1.97[b]
C(3)–Re(1)–C(2)	90.5(9)	C(3)–Re(1)–C(1)	87.5(12)
C(2)–Re(1)–C(1)	83.2(10)	C(3)–Re(1)–S(3)	89.7(8)
C(2)–Re(1)–S(3)	89.0(7)	C(1)–Re(1) –S(3)	171.6(8)
C(3)–Re(1)–S(1)	169.3(8)	C(2)–Re(1)–S(1)	97.7(7)
C(1)–Re(1)–S(1)	100.3(9)	S(3)–Re(1)–S(1)	83.5(2)
C(3)–Re(1)–S(2)	97.8(7)	C(2)–Re(1)–S(2)	167.7 (7)
C(1)–Re(1)–S(2)	106.2(7)	S(3)–Re(1)–S(2)	82.0(2)
S(1)–Re(1)–S(2)	73.06(14)	C(3)–Re(1)–Re(2)	125.6(7)
C(2)–Re(1)–Re(2)	127.6(7)	C(1)–Re(1)–Re(2)	64.7(8)
S(3)–Re(1)–Re(2)	123.00(14)	S(1)–Re(1)–Re(2)	53.37(10)
S(2)–Re(1)–Re(2)	53.35(10)	C(6)–Re(2)–C(5)	91.9(9)
C(6)–Re(2)–C(4)	89.4(9)	C(5)–Re(2)–C(4)	89.3(9)
C(6)–Re(2)–S(1)	105.8(5)	C(5)–Re(2)–S(1)	95.5(6)
C(4)–Re(2)–S(1)	163.8(7)	C(6)–Re(2)–S(2)	104.2(6)
C(5)–Re(2)–S(2)	162.6(6)	C(4)–Re(2)–S(2)	97.1(6)
S(1)–Re(2)–S(2)	74.17(14)	C(6)–Re(2)–Re(1)	152.0(5)
C(5)–Re(2)–Re(1)	108.2(6)	C(4)–Re(2)–Re(1)	109.5(7)
S(1)–Re(2)–Re(1)	54.33(11)	S(2)–Re(2)–Re(1)	54.41(10)
C(9)–Re(3)–C(8)	84.7(9)	C(9)–Re(3)–C(7)	94.0(10)
C(8)–Re(3)–C(7)	87.9(10)	C(9)–Re(3)–S(3)	177.0(6)
C(8)–Re(3)–S(3)	95.4(6)	C(7)–Re(3)–S(3)	89.1(9)
C(9)–Re(3)–S(1)	94.8(6)	C(8)–Re(3)–S(1)	99.6(7)
C(7)–Re(3)–S(1)	168.9(9)	S(3)–Re(3)–S(1)	82.2(2)
C(9)–Re(3)–S(2)	98.9(6)	C(8)–Re(3)–S(2)	171.1(7)
C(7)–Re(3)–S(2)	99.9(8)	S(3)–Re(3)–S(2)	80.6(2)
S(1)–Re(3)–S(2)	72.08(14)	C(10)–Re(4)–C(11)	85.6(9)
C(10)–Re(4)–C(13)	91.7(10)	C(11)–Re(4)–C(13)	88.6(9)
C(10)–Re(4)–C(12)	92.5(10)	C(11)–Re(4)–C(12)	177.8(8)
C(13)–Re(4)–C(12)	90.3(9)	C(10)–Re(4)–C(23)	90.2(9)
C(11)–Re(4)–C(23)	85.5(8)	C(13)–Re(4)–C(23)	173.5(8)
C(12)–Re(4)–C(23)	95.8(9)	C(10)–Re(4)–S(1)	175.5(7)
C(11)–Re(4)–S(1)	96.7(5)	C(13)–Re(4)–S(1)	84.5(6)
C(12)–Re(4)–S(1)	85.1(7)	C(23)–Re(4)–S(1)	93.8(5)
C(17)–Re(5)–C(16)	90.4(12)	C(17)–Re(5)–C(15)	88.6(10)
C(16)–Re(5)–C(15)	91.9(11)	C(17)–Re(5)–C(14)	88.2(11)
C(16)–Re(5)–C(14)	176.6(10)	C(15)–Re(5)–C(14)	85.0(12)
C(17)–Re(5)–C(18)	91.3(8)	C(16)–Re(5)–C(18)	91.5(9)
C(15)–Re(5)–C(18)	176.6(10)	C(14)–Re(5)–C(18)	91.6(9)
C(17)–Re(5)–S(2)	174.3(8)	C(16)–Re(5)–S(2)	85.3(8)
C(15)–Re(5)–S(2)	87.8(8)	C(14)–Re(5)–S(2)	95.9(6)
C(18)–Re(5)–S(2)	92.5(5)	Re(2)–S(1)–Re(1)	72.30(13)
Re(2)–S(1)–Re(3)	102.3(2)	Re(1)–S(1)–Re(3)	84.98(14)
Re(2)–S(1)–Re(4)	126.9(2)	Re(1)–S(1)–Re(4)	121.4(2)
Re(3)–S(1)–Re(4)	128.3(2)	Re(2)–S(2)–Re(1)	72.23(12)
Re(2)–S(2)–Re(3)	102.1(2)	Re(1)–S(2)–Re(3)	84.79(13)
Re(2)–S(2)–Re(5)	128.8(2)	Re(1)–S(2)–Re(5)	123.0(2)
Re(3)–S(2)–Re(5)	126.1(2)	Re(1)–S(3)–Re(3)	85.9(2)
C(18)–N(1)–C(19)	125(2)	C(18)–N(1)–C(20)	122(2)
C(19)–N(1)–C(20)	113(2)	C(18)–N(2)–C(21)	131(2)
C(18)–N(2)–C(22)	121(2)	C(21)–N(2)–C(22)	108(2)
C(24)–N(3)–C(23)	127(2)	C(24)–N(3)–C(25)	113(2)
C(23)–N(3)–C(25)	119(2)	C(23)–N(4)–C(27)	131(2)
C(23)–N(4)–C(26)	124(2)	C(27)–N(4)–C(26)	106(2)
N(1)–C(18)–N(2)	120(2)	N(1)–C(18)–Re(5)	121(2)
N(2)–C(18)–Re(5)	119(2)	N(4)–C(23)–N(3)	114(2)
N(4)–C(23)–Re(4)	128(2)	N(3)–C(23)–Re(4)	119(2)

Average values for [a] Re(1), Re(2) and Re(3), and [b] Re(4) and Re(5).

The solid state structure of **8** is shown in Fig. 1, and selected bond distances and angles in Table 4. The structure of the cluster consists of five rhenium atoms, two μ_4-S, one μ-SH, two tetramethyldiaminocarbene and 17 terminal carbonyl ligands. The central part of the cluster consists of a distorted Re_3S_3 octahedral unit with meridonal arrangement of three rhenium [Re(1), Re(2), Re(3)] and the three sulfur atoms. Two of the sulfur atoms [S(1), S(2)] are each bound to the three rhenium atoms at the centre and also bonded to a terminally placed $Re(CO)_4\{C(NMe_2)_2\}$ moiety, the third sulfur atom [S(3)] belongs to a SH group which bridges a pair of the meridonal rhenium atoms [Re(1), Re(3)]. Each of the remote rhenium atoms [Re(4) and Re(5)] contains four carbonyl ligands while the central rhenium atoms contain three carbonyl ligands each. Out of the three meridonal rhenium atoms, only two Re(1) and Re(2) are mutually bonded indicating that the Re–Re bonds in $[Re_2(CO)_{10}]$ have also been cleaved during the formation of **8**. The Re(1)–Re(2) bond length of 2.9334(12) Å is significantly shorter compared to the Re–Re bond length of 3.041(1) Å in $[Re_2(CO)_{10}]$ [28]. This shortening is probably due to the two μ_4-S ligands, of which S(1) is bonded to the Re(l), Re(2), Re(3) and Re(4) atoms while S(2) is bonded to Re(l), Re(2) Re(3) and Re(5). The μ-SH ligand bridges the nonbonded Re(1) and Re(3) atoms causing a compression in the Re(l)···Re(3) distance [3.3986(12) Å] compared to the other nonbonded distance Re(2)···Re(3) [3.8951(12) Å].

The coordination of the bridging SH group is slightly asymmetrical, Re(3)–S(3) = 2.512(6) and Re(1)–S(3) = 2.474(6) Å. The Re–S bond lengths involving the sulfido atoms also show variations from 2.471(4) to 2.543(4) Å. The average Re–S distance 2.508 Å is close those observed in other complexes, e.g. $[Re_2(CO)_9(\eta^1\text{-}SCHCMe_2CH_2)]$ {2.485(4) Å} [29], $[Re_2(CO)_9(\eta^1\text{-}SCH_2CH_2CH_2SCH_2CH_2CH_2SCH_2CH_2CH_2)]$ {2.498(3) Å} [30], $[Re_2(CO)_9]\{\eta^1\text{-}SC(NEt_2)N(H)(p\text{-}tolyl\}]$ {2.532(3) Å} [21] and $[Ru_4(CO)_6(\mu\text{-}CO)_3(\mu_4\text{-}S)_2\{C(NH^iPr)_2\}]$ {2.5282(13) and 2.5662(13) Å} [14]. It is noted that the Re–S bonds involving the terminal rhenium atoms [2.541(4), 2.542(4) Å] are somewhat longer than those involving the meridonal atoms [2.471(4)–2.536(5), average 2.500 Å]. Similar trend is also reflected in the Re–C(CO) distances, with Re(4)/Re(5)–C bonds [1.91(2)–2.00(2), average 1.97 Å] being ca. 0.08 Å longer than those involving the meridonal rhenium atoms [1.79(2)–1.94(2), average 1.89 Å]. This apparent increase in the effective radius of the terminal rhenium atoms may be caused by the higher electron density at Re(4) and Re(5) due to the bonding of the tetramethyldiaminocarbene ligands. Of the five rhenium atoms, only one [Re(1)] is seven-coordinate, whilst the others are all six-coordinate. The six-coordinate atoms are octahedral with considerable distortions due to the

Table 5
Selected bond lengths (Å) and angles (°) for $[Re_5(CO)_{17}(\mu_4\text{-}S)_2(\mu\text{-}OH)\{C(NMe_2)_2\}_2]$ **9**

Re(1)–Re(2)	2.9903(10)	Re(1)–O(18)	2.124(10)
Re(1)–S(1)	2.499(4)	Re(1)–S(2)	2.513(4)
Re(2)–S(1)	2.466(3)	Re(2)–S(2)	2.467(3)
Re(3)–O(18)	2.196(10)	Re(3)–S(1)	2.527(3)
Re(3)–S(2)	2.536(4)	Re(4)–C(23)	2.26(2)
Re(4)–S(1)	2.530(4)	Re(5)–C(18)	2.231(14)
Re(5)–S(2)	2.534(4)		
Re–C(CO)	1.89^a	Re–C(CO)	1 97^b
C(3)–Re(1)–C(2)	88.2(7)	C(3)–Re(1)–C(1)	86.7(9)
C(2)–Re(1)–C(1)	79.7(8)	C(3)–Re(1)–O(18)	92.9(7)
C(2)–Re(1)–O(18)	94.3(6)	C(1)–Re(1)–O(18)	173.9(6)
C(3)–Re(1)–S(1)	169.1(5)	C(2)–Re(1)–S(1)	100.1(5)
C(1)–Re(1)–S(1)	101.6(7)	0(18)–Re(1)–S(1)	79.6(3)
C(3)–Re(1)–S(2)	97.4(4)	C(2)–Re(1)–S(2)	171.3(5)
C(1)–Re(1)–S(2)	107.1(6)	0(18)–Re(1)–S(2)	79.0(3)
S(1)–Re(1)–S(2)	73.46(12)	C(3)–Re(1)–Re(2)	126.6(6)
C(2)–Re(1)–Re(2)	128.3(5)	C(1)–Re(1)–Re(2)	67.7(7)
0(18)–Re(1)–Re(2)	117.0(3)	S(1)–Re(1)–Re(2)	52.46(8)
S(2)–Re(1)–Re(2)	52.39(8)	C(6)–Re(2)–C(5)	88.2(8)
C(6)–Re(2)–C(4)	90.5(8)	C(5)–Re(2)–C(4)	90.1(7)
C(6)–Re(2)–S(1)	106.3(5)	C(5)–Re(2)–S(1)	96.2(5)
C(4)–Re(2)–S(1)	162.3(6)	C(6)–Re(2)–S(2)	104.7(5)
C(5)–Re(2)–S(2)	165.8(6)	C(4)–Re(2)–S(2)	95.5(5)
S(1)–Re(2)–S(2)	74.85(12)	C(6)–Re(2)–Re(1)	151.4(5)
C(5)–Re(2)–Re(1)	112.0(6)	C(4)–Re(2)–Re(1)	108.8 (6)
S(1)–Re(2)–Re(1)	53.48(9)	S(2)–Re(2)–Re(1)	53.81(8)
C(9)–Re(3)–C(7)	91.4(8)	C(9)–Re(3)–C(8)	88.0(7)
C(7)–Re(3)–C(8)	86.4(8)	C(9)–Re(3)–O(18)	172.1(5)
C(7)–Re(3)–O(18)	94.8(6)	C(8)–Re(3)–O(18)	97.2(6)
C(9)–Re(3)–S(1)	95.5(5)	C(7)–Re(3)–S(1)	170.2(6)
C(8)–Re(3)–S(1)	100.7(5)	0(18)–Re(3)–S(1)	77.7(3)
C(9)–Re(3)–S(2)	97.0(5)	C(7)–Re(3)–S(2)	99.8(6)
C(8)–Re(3)–S(2)	171.9(5)	0(18)–Re(3)–S(2)	77.2(3)
S(1)–Re(3)–S(2)	72.60(11)	C(10)–Re(4)–C(13)	93.4(8)
C(10)–Re(4)–C(11)	86.2(8)	C(13)–Re(4)–C(11)	88.1(7)
C(10)–Re(4)–C(12)	91.2(9)	C(13)–Re(4)–C(12)	91.9(7)
C(11)–Re(4)–C(12)	177.4(7)	C(10)–Re(4)–C(23)	91.2(7)
C(13)–Re(4)–C(23)	172.7(7)	C(11)–Re(4)–C(23)	86.6(6)
C(12)–Re(4)–C(23)	93.7(6)	C(10)–Re(4)–S(1)	174.9(6)
C(13)–Re(4)–S(1)	82.1(5)	C(11)–Re(4)–S(1)	96.0(4)
C(12)–Re(4)–S(1)	86.5(5)	C(23)–Re(4)–S(1)	93.6(5)
C(17)–Re(5)–C(15)	91.4(9)	C(17)–Re(5)–C(14)	88.9(9)
C(15)–Re(5)–C(14)	84.0(9)	C(17)–Re(5)–C(16)	91.6(10)
C(15)–Re(5)–C(16)	92.7(9)	C(14)–Re(5)–C(16)	176.7(7)
C(17)–Re(5)–C(18)	90.9(7)	C(15)–Re(5)–C(18)	173.9(8)
C(14)–Re(5)–C(18)	90.4(6)	C(16)–Re(5)–C(18)	92.9(6)
C(17)–Re(5)–S(2)	174.4(6)	C(15)–Re(5)–S(2)	85.6(6)
C(14)–Re(5)–S(2)	95.4(5)	C(16)–Re(5)–S(2)	83.9(6)
C(18)–Re(5)–S(2)	92.7(4)	Re(2)–S(1)–Re(1)	74.06(10)
Re(2)–S(1)–Re(3)	102.24(13)	Re(1)–S(1)–Re(3)	82.16(10)
Re(2)–S(1)–Re(4)	127.56(14)	Re(1)–S(1)–Re(4)	121.1(2)
Re(3)–S(1)–Re(4)	128.15(14)	Re(2)–S(2)–Re(1)	73.81(10)
Re(2)–S(2)–Re(5)	128.9(2)	Re(1)–S(2)–Re(5)	122.6(2)
Re(2)–S(2)–Re(3)	101.97(13)	Re(1)–S(2)–Re(3)	81.71(10)
Re(5)–S(2)–Re(3)	126.77(14)	Re(1)–O(18)–Re(3)	99.7(4)
C(18)–N(1)–C(19)	125.8(13)	C(18)–N(1)–C(20)	121(2)
C(19)–N(1)–C(20)	112(2)	C(18)–N(2)–C(22)	122(2)
C(18)–N(2)–C(21)	128(2)	C(22)–N(2)–C(21)	110(2)
C(23)–N(3)–C(24)	124(2)	C(23)–N(3)–C(25)	120(2)
C(24)–N(3)–C(25)	114(2)	C(23)–N(4)–C(27)	124(2)
C(23)–N(4)–C(26)	124.2(14)	C(27)–N(4)–C(26)	112(2)
N(1)–C(18)–N(2)	116(2)	N(1)–C(18)–Re(5)	122.6(11)
N(2)–C(18)–Re(5)	121.5(12)	N(4)–C(23)–N(3)	113(2)
N(4)–C(23)–Re(4)	126.2(12)	N(3)–C(23)–Re(4)	120.3(14)

Average values for ^{a}Re(1), Re(2) and Re(3), and ^{b}Re(4) and Re(5).

bridging bonds and steric factors. The geometry around Re(1) may also be considered as octahedral with the seventh ligand [Re(2)] capping the trigonal face defined by S(1), S(2) and C(1). The tetramethyldiaminocarbene ligands bonded to the two terminal metals are both *cis* with respect to the sulfido groups.

The ^{1}H and IR spectra of **8** are consistent with its solid state structure established by X-ray diffraction methods. The ^{1}H-NMR spectrum shows two singlets at δ 3.28 and 1.85 with a relative intensity of 24:1. The singlet at δ 3.28 is assigned to the methyl protons of the tetramethyldiaminocarbene ligands while the singlet at δ 1.85 is due to the μ-SH proton. Utilizing the X-ray structure of **8** we can explain the equivalence of the methyl groups of the tetramethyldiaminocarbene ligands. Since there are free rotations of Re(4)–S(1) and Re(5)–S(2) bonds, the tetramethyl groups of the carbene moieties bonded to Re(4) and Re(5) atoms become equivalent. As expected the IR spectrum of **8** in the carbonyl stretching region in CH_2Cl_2 shows absorptions at 2098m, 2070w, 2060w, 2033m, 2014vs, 1989m, 1950sh, 1934s 1910s and 1892sh cm^{-1}.

The IR spectrum of **9** in the carbonyl region is very similar to that of **8** suggesting that compounds **8** and **9** are isostructural. In the ^{1}H-NMR spectrum the singlet at δ 3.34 is due to the methyl groups of the tetramethyldiaminocarbene ligands while the high field singlet at δ -1.25 is assigned to the hydrogen of the bridging OH group. Similar high field ^{1}H-NMR signals have been reported for the bridging OH proton of bimetallic clusters [19,31,32].

The solid state structure of **9** is shown in Fig. 2, and selected bond distances and angles in Table 5. The structure of **9** is very similar to that of **8** in regard to the number and arrangement of the metal atoms, μ_4-S, tetramethyldiaminocarbene and carbonyl ligands with the only exception that the μ-SH ligand in **8** has been replaced by a μ-OH ligand in **9**. The bond distances and angles in **9** are comparable with the corresponding values in **8**, showing only small differences except those caused by the difference in the radii of the bridging sulfur and oxygen atoms in **8** and **9**, respectively. Thus the Re(1)–Re(3) and Re(1)–Re(3) distances, 2.9903(10) and 3.3029(10) Å, respectively, in **9** show significant variations from the corresponding values [2.9334(12) and 3.3986(12) Å] in **8**, whilst the Re(2)–Re(3) distance, least affected by the SH or OH bridging, has a value of 3.8872(10) Å compared with 3.8951(12) Å in **8**. The corresponding Re–S bond distances involving the sulfido ligands are virtually the same as in **8** and follow the same pattern. These distances range from 2.466(3) to 2.536(4) Å and have an average of 2.509 Å. As expected, the Re–S–Re angles in **9** show considerable variations from the tetrahedral value (109.5°); those involving the meridonal rhenium atoms lie in the range 73.81(10)–102.24(12)°, whilst those involving the termi-

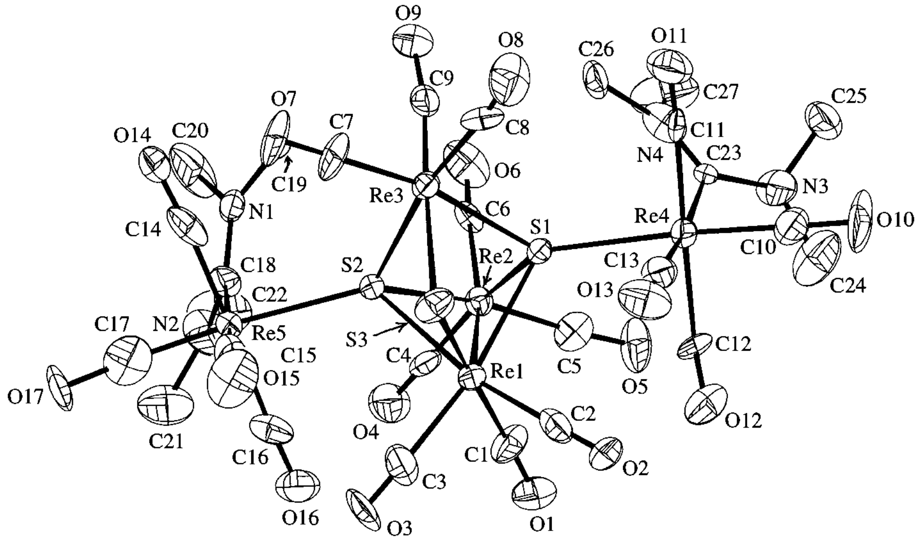


Fig. 1. Solid state structure of $[\mathrm{Re_5(CO)_{17}}(\mu_4\text{-S})_2(\mu\text{-SH})\{\mathrm{C(NMe_2)_2}\}_2]$ **8** showing the atom labelling scheme. Thermal ellipsoids are drawn at 45% probability. The hydrogen atoms are omitted for clarity.

nal atoms fall in the range 121.1(2)–128.9(2)°. These values are very similar to those, 72.23(12)–102.3(2) and 121.4(2)–128.9(2)°, respectively, found in **8**. The Re–C(CO) distances are also comparable with the corresponding values in **8** and follow the same pattern, i.e. the values are longer for the terminal compared with the meridonal rhenium atoms [1.854(13)–1.902(13), average 1.89 Å vs 1.902(14)–2.02(2), average 1.97 Å].

The two Re–OH distances in **9** are Re(1)–O(18) = 2.124(10) and Re(3)–O(18) = 2.196(10) Å. These values are comparable to those reported for bridging hydroxy groups in $[(\mu\text{-H})\mathrm{Os(CO)_9}[(\mu\text{-OH})(\mathrm{PMe_2Ph})]$ {2.135(5), 2.118(5) Å} [31], $[(\mu\text{-H})\mathrm{Os_3(CO)_8}[(\mu\text{-OH})(\mu\text{-dppm})]$ {2.1678(8), 2.157(8) Å} [32], $[\mathrm{Os_3(CO)_9}[(\mu\text{-OH})(\mu\text{-OMeOCO})\{\eta^1\text{-SC(NMe}_2)\}]$ {2.148(8), 2.084(9) Å} [19] and $[(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-OH})]$ {2.146(7), 2.136(7) Å} [33]. The Re(1)–O(18)–Re(3) bridge angle in **9** is obtuse [99.7(4)°] in contrast with the Re(1)–S(3)–Re(3) bridge angle in **8** which is acute [85.9(2)°]. The Re(4)–C(23) and Re(5)–C(18) distances {2.26(2), 2.24(2) Å in **8**; 2.26(2), 2.231(14) Å in **9**}, despite the carbenoid character, are significantly longer than the diaminocarbene-metal bonds in $[(\mu\text{-H})\mathrm{Ru_3(CO)_8}(\mu_3\text{-S})(\eta^2\text{-CH}_2\mathrm{CMe_2NHCNHBu^t})]$ {2.108(3) Å}, $[(\mu\text{-H})\mathrm{Ru_3(CO)_9}(\mu_3\text{-S–Ru(CO)}_3)(\eta^2\text{-CH}_2\mathrm{CMe_2NHCNHBu^t})]$ {2.087(4) Å} [16], $[\mathrm{Ru_4(CO)_6}\text{-}(\mu\text{-CO})_3((\mu_4\text{-S})_2\{\mathrm{C(NH^iPr)}\}_2]$ {2.094(5), 2.068(5) Å} [14], $[\mathrm{Ru_4(CO)_7}(\mu\text{-CO})_3(\mu_4\text{-S})_2\{\mathrm{C(NH^iPr)}\}_2]$ {2.099(3) Å} [14] and $[\mathrm{Ru_6(CO)_{14}}(\mu\text{-CO})_2(\mu_4\text{-S})\{\mu_3\text{-}\eta^2\text{-EtNCSNHEt}\}(\mu_3\text{-}\eta^2\text{-EtNCNHEt})]$ {2.10(2) Å} [15]. The dimen-

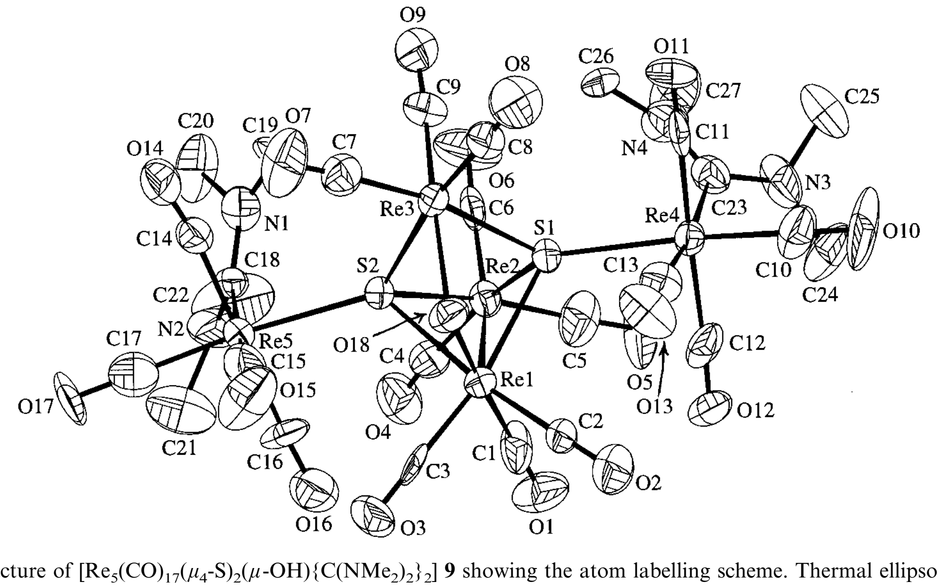


Fig. 2. Solid state structure of $[\mathrm{Re_5(CO)_{17}}(\mu_4\text{-S})_2(\mu\text{-OH})\{\mathrm{C(NMe_2)_2}\}_2]$ **9** showing the atom labelling scheme. Thermal ellipsoids are drawn at 45% probability. The hydrogen atoms are omitted for clarity.

sions of the tetramethyldiaminocarbene ligands are as expected for this type of species.

The C–N distances reveal a partial double bond character [C(18)–N(1) = 1.32(3), C(18)–N(2) = 1.34(3), C(23)–N(3) = 1.38(3), C(23)–N(4) = 1.27(3) Å for **8** and C(18)–N(1) = 1.30(2), C(18)–N(2) = 1.34(3), C(23)–N(3) = 1.37(2), C(23)–N(4) = 1.33(2) Å for **9**] and are close to the values found in several ruthenium clusters containing diaminocarbene ligands [14–16]. In both compounds, the carbene atoms C(18) and C(23) as well as the amino nitrogens are nearly planar, with the latter showing small pyramidal distortions. The two NMe_2 groups in each ligand are mutually rotated by 41(1)° for C(18) and 49(1)° for C(23) in **9**, with very similar values 40(1) and 52(2)° in **8**. There are considerable variations in the N–C–N and C–N–C angles from the ideal trigonal value of 120° which are presumably caused by steric crowding.

It is suggested that during photolysis, the Re–Re bond in $[Re_2(CO)_{10}]$ is cleaved generating various coordantively unsaturated $Re(CO)_n$ moieties; the C=S bond of tetramethylthiourea is also cleaved and during the recombination processes of these species an oxygen atom is abstracted from trace of moisture present in the solvent giving **9**. The number of transition-metal cluster compounds containing two diaminocarbene ligands is still rather limited. To our knowledge compounds **8** and **9** are the first examples of pentanuclear rhenium compounds containing two diaminocarbene, one μ-EH (E = S, O), two μ_4-S and 17 carbonyl ligands.

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