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The Spectroscopic Characterization of Tungsten(V) Complexes of the Type $Cp_2W_2(\mu\text{-}S)_2EE'$. Crystal and Molecular Structure of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$

MAX HERBERHOLD*, WOLFGANG JELLEN
Laboratorium für Anorganische Chemie der Universität, D-8580 Bayreuth, F.R.G.

and MANFRED L. ZIEGLER
Anorganisch-chemisches Institut der Universität, D-6900 Heidelberg, F.R.G.

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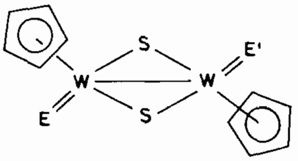
Abstract

The binuclear, sulfur-bridged tungsten complexes $Cp_2W_2(\mu\text{-}S)_2E_2$ (E = $NSiMe_3$ (**1**), O (**2**) and S (**3**)) and $Cp_2W_2(\mu\text{-}S)_2EE'$ (E = $NSiMe_3$, E' = O (**4**); E = $NSiMe_3$, E' = S (**5**); E = O, E' = S (**6**)) were obtained in low yields from the reactions of bis(trimethylsilyl)sulfur diimide, $S(NSiMe_3)_2$, with cyclopentadienyl tungsten compounds such as $CpW(CO)_3Cl$ and $[CpW(CO)_3]_2$. The molecular stereochemistry of **1** was determined by a three-dimensional X-ray diffraction study. The centrosymmetric molecules of **1** contain a planar $W_2(\mu\text{-}S)_2$ ring (W–W 2.903(3) Å, S•••S 3.651(7) Å, angle WSW 77.0(1)°) and terminal 4-electron imido ligands $N(SiMe_3)$ (angle WNSi 170.9(25)°). Complexes **1–6** were characterized by their IR, ^1H and ^{13}C NMR and mass spectra.

Introduction

In our investigations of the reactions of bis(trimethylsilyl)sulfur diimide, $S(NSiMe_3)_2$, with cyclopentadienyl-tungsten compounds such as $[CpW(CO)_3]_2$ and $CpW(CO)_3Cl$, the formation of binuclear complexes containing two sulfur bridges was observed**. We describe the spectroscopic characterization of these low-yield by-products (**1–6**) to which a structure **A** with a planar $W(\mu\text{-}S)_2W$ core is ascribed. The molecular structure of the new bis(trimethylsilylimido) complex, $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**), was determined by an X-ray crystallographic analysis.



A

1: E = E' = $NSiMe_3$
2: E = E' = O
3: E = E' = S
4: E = $NSiMe_3$; E' = O
5: E = $NSiMe_3$; E' = S
6: E = O; E' = S

Experimental

Materials

The cyclopentadienyl tungsten complexes $[CpW(CO)_3]_2$ [1], $CpW(CO)_3Cl$ [2] and $CpW(CO)_3SH$ [3] were prepared according to literature procedures. Bis(trimethylsilyl)sulfur diimide, $S(NSiMe_3)_2$, was obtained from the reaction of $LiN(SiMe_3)_2$ with $SOCl_2$ [4]. Trimethylsilyl azide, Me_3SiN_3, was purchased from Fluka.

The binuclear sulfur-bridged tungsten complexes $Cp_2W_2(\mu\text{-}S)_2O_2$ (**2**) [5] and $Cp_2W_2(\mu\text{-}S)_2S_2$ (**3**) [3, 6] have been described previously.

Reactions

All manipulations were carried out under an inert atmosphere of prepurified dinitrogen. Solvents were dried and distilled (THF, benzene and cyclohexane from Na/K alloy, dichloromethane from P_4O_{10}) under an atmosphere of dinitrogen.

(a) Reaction of $CpW(CO)_3Cl$ with $S(NSiMe_3)_2$

The main product of the reaction of $CpW(CO)_3Cl$ (0.74 g, 2 mmol) with an excess of $S(NSiMe_3)_2$ (1.65 g, 1.87 ml, 8 mmol) in boiling THF (50 ml)

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*Author to whom correspondence should be addressed.

**Abbreviations: Cp = η^5-cyclopentadienyl, η^5-C_5H_5; Cp* = η^5-pentamethylcyclopentadienyl, η^5-C_5Me_5.

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is a black material which is insoluble in organic solvents [3, 6, 7]; it varies in sulfur content. Extraction of the black polymer with CH_2Cl_2 gives a yellow solution which contains small amounts of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**) and $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)(S)$ (**5**). Separation of the two complexes by thin-layer chromatography (TLC) (silica gel, cyclohexane/THF 9:1) gave 8 mg (1%) **1** and 5 mg (0.7%) **5**. *Anal.* **1** Found: N, 3.46; S, 8.46; W, 49.90. Calc. for $C_{16}H_{28}N_2S_2Si_2W_2$ (736.4): N, 3.80; S, 8.71; W, 49.93%.

(b) Reaction of [CpW(CO)₃]₂ with S(NSiMe₃)₂

A solution of $[CpW(CO)_3]_2$ (1.33 g, 2 mmol) and $S(NSiMe_3)_2$ (1.03 g, 1.17 ml, 5 mmol) in benzene (80 ml) was kept at 100 °C in a 100 ml-autoclave for 6 days. The black reaction mixture was then brought to dryness and the residue extracted with CH_2Cl_2. Separation by TLC (as under (a)) gave 30 mg (2%) **1** and 14 mg (1%) **5**.

(c) Reaction of CpW(CO)₃SH with trimethylsilyl azide

The sulfhydryl tungsten complex $CpW(CO)_3SH$ (0.37 g, 1 mmol), and trimethylsilyl azide, Me_3SiN_3 (0.115 g, 0.13 ml, 1 mmol) were dissolved in THF (40 ml) and the solution heated to 100 °C in a 100 ml-autoclave for 24 h. The solvent was removed, the remaining brown oil was dissolved in 1 ml CH_2Ci_2 and chromatographed on silica gel at –20 °C. Elution with CH_2Ci_2/pentane (1:1) gave a red zone containing 73 mg (22%) $[CpW(CO)_3]_2$. Subsequent elution with CH_2Cl_2 produced an orange band containing 37 mg (11%) **5**.

(d) Hydrolysis of 1 and 5

The terminal trimethylsilylimido ligands in **1** are hydrolytically cleaved in the presence of dilute acid (HCl, H_2SO_4) to give yellow $Cp_2W_2(\mu\text{-}S)_2O_2$ (**2**) [5] in a quantitative reaction. The yellow intermediate $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)(O)$ (**4**) is occasionally obtained (in small amounts) upon TLC purification of **1**.

The analogous hydrolysis of **5** by acid leads to the quantitative formation of orange $Cp_2W_2(\mu\text{-}S)_2(O)(S)$ (**6**). For example, 37 mg (0.05 mmol) **5** were dissolved in CH_2Ci_2 (5 ml) and dilute sulfuric acid (5 ml) was added. The two-layer mixture was vigorously stirred at 50 °C for 3 h and **6** was isolated from the CH_2Cl_2 layer and purified by TLC. Yield 32 mg (97%).

Instrumentation

The following spectrometers were available. Infrared: Beckman 4240 (KBr). ^1H and ^{13}C NMR: Jeol FX 90 Q; Mass: Varian MAT CH7 (ionization energy 70 eV).

TABLE I. Crystal Data of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**)

Formula	$C_{16}H_{28}N_2S_2Si_2W_2$
M_r	736.4
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell parameters	
a (A)	7.480(5)
b (A)	9.33(3)
c (A)	16.60(2)
β (°)	94.85(8)
V (A^3)	1154.8
Z	2
D_c (g cm^{-3})	2.12
$F(000)$	692
μ	98.1
Number of reflections (refinement)	2542(2515)
Maximum shift/e.s.d.	–0.09 (C(7), U33), average 0.02
Largest feature in final difference Fourier map (e A^3)	0.3 and –0.64
R_{iso}	0.084
R_{aniso}	0.054
R_w	0.045

X-ray Crystallography (Table I)

Single crystals of **1** were obtained from dichloromethane solution layered with pentane. A yellow crystal (0.3 × 0.2 × 0.2 mm) mounted on top of a glass capillary was used for this investigation. Lattice parameters were derived from setting angles of 39 machine-centered reflections (Siemens-Stoe AEDII, monochromatic Mo Kα radiation). Data collection (ω scans, $2\theta \leqslant 65°$, index ranges $0 \leqslant h \leqslant 7$, $0 \leqslant k \leqslant 8$ and $-15 \leqslant l \leqslant 15$) yielded 2542 observed independent reflections with $I > 1.5\sigma(I)$ (2514 unique reflections); equivalent reflections merged ($R_{int} = 8.3$). Two standard reflections were measured every 2 h, no significant fluctuations being observed. Lorentz and polarisation corrections as well as an empirical (ψ scans of 4 reflections with $10° < 2\theta < 22°$, minimum transmission 0.42 (maximum = 1.00)) absorption corrections were applied.

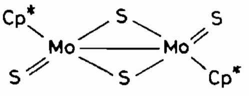
The crystal system is monoclinic with space group $P2_1/n$ and $Z = 2$, which means that the discrete molecules must possess a center of symmetry. The structure was solved by Patterson and Fourier maps; a difference Fourier map enabled the location of all hydrogen atoms. Final refinement by a block-matrix procedure based on F (non-hydrogen atoms with anisotropic temperature factors) converged with a weighted $R_w = 0.045$ (unweighted $R = 0.054$, $R_w = \Sigma|F_o - F_c|\sqrt{w}|\Sigma F_o\sqrt{w}$, $w = 1/\sigma^2(F)$). Calculations were carried out on a Data General 'Eclipse'-computer; the program packages were COSY 85 [7] and STRUCSY [8] (refinement). Scattering factors including anomalous dispersion are from International Tables for X-ray Crystallography [9].

Results and Discussion

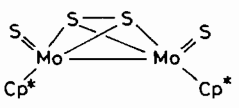
Structure and Configuration of the Complexes

Binuclear compounds of the type $Cp_2M_2(\mu\text{-}S)_2E_2$ are known for M = Mo and W, but not for M = Cr. They were extensively investigated in the molybdenum series where several X-ray crystallographic structures were reported, e.g. for $Cp_2Mo_2(\mu\text{-}S)_2E_2$ (E = N^tBu [11], O [12] and S [3, 6]), $(C_5H_4Me)_2Mo_2(\mu\text{-}S)_2E_2$ (E = S [10]) and $(C_5Me_5)_2Mo_2(\mu\text{-}S)_2E_2$ (E = O [10, 13] and S [10]). In all these cases the central $Mo(\mu\text{-}S)_2Mo$ unit is planar; both the five-membered cyclopentadienyl rings and the two ligands E are arranged *trans* to each other with respect to the $Mo(\mu\text{-}S)_2Mo$ plane, *i.e.* the complexes possess the centrosymmetric *anti*-configuration (**A**). The first *tungsten* complex of this type to be characterized structurally, $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**), has an analogous configuration (see below).

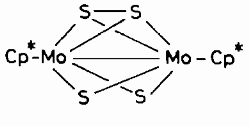
Other isomers of the $Cp_2M_2S_2E_2$ (M = Mo, W) group of complexes are known [10, 14], but less well documented structurally; the variety of structures appears to be largest in the series of pentamethylcyclopentadienyl complexes [10, 14]. The *syn*-configuration (**B**) in which the two rings are arranged *cis* to each other has been characterized in *syn*-$Cp^*{}_2Mo_2(\mu\text{-}S)_2O_2$ [13]; the central Mo_2S_2 unit is non-planar. The bridging sulfur ligands may act either as two single μ-S bridges or as one μ-S_2 bridge. An isomer without terminal chalcogeno ligands (**C**) has been verified structurally in $Cp^*{}_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$ [14]; again, either individual sulfido (μ-S) or disulfido (μ-S_2) bridges are possible. The Mo–Mo distance is apparently reduced on going from structure **A** to **B**, and further shortened on going from **B** to **C**. The photochemical interconversion of three isomers of the types **A**, **B** and **C** has been studied in the case of the sulfido complexes $Cp^*{}_2Mo_2S_4$ [15].



$(C_5Me_5)_2Mo_2(\mu\text{-}S)_2S_2$
(*anti*) [10]
A

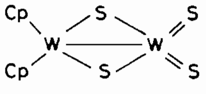


$(C_5Me_5)_2Mo_2(\mu\text{-}S)_2S_2$
(*syn*)
B



$(C_5Me_5)_2Mo_2(\mu\text{-}S)_2(\mu\text{-}S_2)$
[14]
C

Unsymmetrical complexes of type **D** such as $Cp_2M(\mu\text{-}S)_2ME_2$ (M = Mo, W; E = O, S) are also known [16]; according to the molecular structure determination carried out for $(Me\text{-}C_5H_4)_2Mo(\mu\text{-}S)_2MoS_2$ [17], the $Mo(\mu\text{-}S)_2Mo$ unit is again planar.



D

Although the isomeric configurations C and **D** may be easily excluded for complexes **1**–**6** on the basis of the IR and NMR data (Table II), the differentiation between *anti*- and *syn*-configurations (**A** and **B**, respectively) is not unequivocally possible by IR and NMR spectroscopy.

However, the assumption that all tungsten complexes (**1**–**6**) possess the *anti*-configuration (**A**) with a planar $W(\mu\text{-}S)_2W$ core is supported by the following two arguments:

(a) The X-ray structure determined for $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**) shows the centrosymmetric *anti*-configuration (**A**). The other complexes (**2**–**6**) are very similar to **1** in their colours (Table II) and thermal stabilities.

(b) The infrared spectra of $Cp_2W_2(\mu\text{-}S)_2S_2$ (**3**) can almost be superimposed on those of the corresponding molybdenum complex the *anti* structure (**A**) of which is known [3, 6].

Compounds of the type $Cp_2M_2(\mu\text{-}S)_2(E)(E')$ (M = W: **4**–**6**) containing two different terminal ligands E and E′ are apparently rare; an example mentioned previously is $Cp^*{}_2Mo_2(\mu\text{-}S)_2(O)(S)$ [10].

Spectroscopic Data of Complexes 1–6 (Table II)

The infrared spectra of **1**–**6** all contain a band of medium intensity at *ca.* 430 cm^{-1} which is assigned to a stretching vibration of the $W_2(\mu\text{-}S)_2$ bridge system. As expected, this absorption appears at lower frequencies than the strong ν(W=S) band of the terminal sulfido ligands (*ca.* 490 cm^{-1}). The assignment of the 430 cm^{-1} absorption to the $W_2(\mu\text{-}S)_2$ core agrees with the earlier assignment [14, 15] for the molybdenum complex $Cp^*{}_2Mo_2(\mu\text{-}S)_2S_2$[‡] and is consistent with the IR characterization of tetrathiometallate complexes such as $[M(MoS_4)_2]^{2-}$ (M = Ni, Fe, Zn) [18], $[M(WS_4)_2]^{2-}$ (M = Ni, Fe, Co, Zn) [19] and similar anions where the terminal metal–sulfido frequencies are always 40–50 cm^{-1} higher than those of the metal–sulfur bridges [20].

The diagnostic stretching absorptions ν(W=E) of the terminal ligands E = $NSiMe_3$, O and S, respectively, are consistently very strong. They are split

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[‡] The following metal–sulfur stretching absorptions were reported for $Cp^*{}_2Mo_2(\mu\text{-}S)_2S_2$: 488s, 444m (Nujol) [10]; 479s, 439w (KBr) [14]; 488s, 447m (KBr) [15]; 486s, 445m ($CHCl_3$ solution, polyethylene cell) [15].

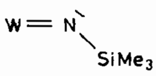
TABLE II. Characteristic Spectroscopic Data of **1**–**6**

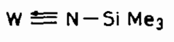
Complex $Cp_2W_2(\mu\text{-}S)_2(E)(E')$	**1** (yellow) $E = E' = NSiMe_3$	**2** (yellow) $E = E' = O$	**3** (brown) $E = E' = S$	**4** (yellow) $E = NSiMe_3; E' = O$	**5** (orange) $E = NSiMe_3, E' = S$	**6** (orange) $E = O, E' = S$
Infrared (KBr) (cm^{-1})						
$\nu(W{=}N)$	1140vs, 1130vs[a]			1130vs	1140vs	
$\nu(W{=}O)$		932s, 920s[b]		925vs		928s
$\nu(W{=}S)$			482s[c]		490s	495s
$\nu(W_2S_2)$	425m	432m	429m	430m	430m	429m
^1H NMR ($CDCl_3$, −20 °C) δ (ppm)						
C_5H_5	5.79	6.15	6.03	6.14; 5.74	6.01; 5.82	6.22; 5.24
$Si(CH_3)_3$	−0.26			−0.23	−0.26	
^{13}C NMR ($CDCl_3$, −20 °C) δ (ppm)						
C_5H_5	100.3	103.3			100.2; 100.8	
$Si(CH_3)_3$	−0.07				−0.05	
Mass *m/e* (I_{rel} (%))[d]						
M^+	736(100)	594(100)	626(100)	665(100)	681(100)	610(100)
$(M - 15)^+$	721(52)			650(98)	666(88)	
$(M - 16)^+$		578(14)		649(94)		594(40)
$(M - 18)^+$		576(14)		647(70)		
$(M - 30)^+$	706(35)			635(17)	651(13)	
$(M - 32)^+$		562(4)	594(6)		649(11)	
$(M - 45)^+$	691(9)			620(20)	636(28)	
$(M - 60)^+$	676(6)					
$(M - 65)^+$		529(19)	561(35)			545(23)
$(M - 73)^+$	663(10)			592(29)	608(9)	
						529(8)
$(M - 91)^+$		503(27)	535(18)	574(41)		519(23)
	633(40)				576(17)	
M^{2+}		297(6)	313(11)			
[e]	338(1)		297(2)		325(23)	
		281(15)	281(1)	318(77)	318(12)	
				288(24)	288(6)	
$SiMe_3^+$	73(83)			73(58)	73(21)	
$C_5H_5^+$	65(4)	65(15)	65(16)	65(54)	65(9)	65(38)
S^+			32(3)		32(44)	32(16)

[a] Only one band is observed in CH_2Cl_2 solution at 1130 cm^{-1}. [b] Only one band is observed in CH_2Cl_2 solution at 929 cm^{-1} (*cf.* ref 5: 910 cm^{-1} (KBr)). [c] *cf.* refs 3, 6: 480 cm^{-1} (KBr). [d] The *m/e* values refer to ^{184}W. [e] Doubly charged ions.

in the solid state spectra of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**) and $Cp_2W_2(\mu\text{-}S)_2O_2$ (**2**), but not of $Cp_2W_2(\mu\text{-}S)_2S_2$ (**3**). In solution (CH_2Cl_2), only one band is observed.

The $\nu(W{=}N)$ frequencies in **1**, **4** and **5** are remarkably high (1130–1140 cm^{-1}), indicating a bond order higher than 2 for the tungsten–nitrogen bond. These compounds are therefore considered to be more 4-electron ('nitrene') than 2-electron ('imido') complexes [21]:


imido complex


nitrene complex

The short W–N bond length (1.743(8) Å) and the large angle at the nitrogen atoms (170.9(25)°) found in $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**) (see below) support the conclusion that the nitrogen atoms are closer to sp than to sp^2 hybridization. Unusually strong metal–nitrogen bonds in 'imido' complexes of transition metals are a general phenomenon [21, 22], and numerous examples have been discussed in the literature (see, e.g. refs. 23–25). The close analogy between imido and oxo ligands [22] suggests that the W=O bonds in **2**, **4** and **6** should also be strong; the importance of triply-bonded (4-electron) oxo ligands in high-valent transition group 6 complexes has been discussed [26].

An estimate of the force constants of the terminal W=E bonds gives values of f = 9.88, 7.43 and 3.74 N cm^{-1} for **1**, **2** and **3**, respectively. Evaluation of the degree of bonding (N) ('Bindungsgrad') according to Badger's rule [27] on the basis of these force constants gives N = 3.80 for **1**; for the molybdenum complexes $Cp_2Mo_2(\mu\text{-}S)_2O_2$ (ν(MoO) 920, 895 cm^{-1} [28], d(MoO), 1.679 Å (average) [12]) and $Cp_2Mo_2(\mu\text{-}S)_2S_2$ (ν(MoS) 482 cm^{-1} [3, 6], d(MoS) 2.144 Å [3, 6]) – which are analogous to **2** and **3** –, degrees of bonding of N = 2.24 and 1.76 can be calculated.

A combination of vibrational and structural data therefore leads to the conclusion that the bond strengths decrease in the series $W{=}NSiMe_3 > W{=}O > W{=}S$.

The ^1H NMR spectra of **1–6** can be used for rapid identification of the complexes since the chemical shifts of the sharp cyclopentadienyl singlets are quite characteristic. All the complexes are diamagnetic.

The mass spectra (Table II) reflect the high stability of the complexes which decompose only above 200 °C: in all cases the peaks of the molecular ion have the highest intensity. Doubly-charged positive ions can be easily recognized by the typical W_2 isotope pattern.

Molecular Structure of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (1)

The solid state structure of **1** was determined by an X-ray crystallographic analysis using single crystals. The structure of an individual molecule is presented in Fig. 1; bond distances and angles are compiled in Table III.

TABLE III. Bond Lengths (Å) and Angles (°) of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**)

W–W′	2.903(3)	Si–N	1.735(9)
W–S	2.334(3)	Si–C(6)	1.852(13)
W–S′	2.330(7)	Si–C(7)	1.857(14)
W–Si	3.467(6)	Si–C(8)	1.846(13)
W–N	1.743(8)		
W–C(1)	2.480(12)	C(1)–C(2)	1.32(3)
W–C(2)	2.476(12)	C(1)–C(5)	1.42(3)
W–C(3)	2.380(11)	C(2)–C(3)	1.39(2)
W–C(4)	2.311(13)	C(3)–C(4)	1.31(2)
W–C(5)	2.336(13)	C(4)–C(5)	1.38(2)
S–W–S′	103(3)	C(2)–C(1)–C(5)	110(1)
S–W–N	102.3(4)	C(1)–C(2)–C(3)	107(2)
S′–W–N	102.7(6)	C(2)–C(3)–C(4)	107(4)
W–S–W′	77.0(1)	C(3)–C(4)–C(5)	110(1)
W–N–Si	170.9(25)	C(1)–C(5)–C(4)	106(1)
N–Si–C(6)	108.2(8)		
N–Si–C(7)	110.2(9)		
N–Si–C(8)	108.9(9)		
C(6)–Si–C(7)	109.3(11)		
C(6)–Si–C(8)	109.6(11)		
C(7)–Si–C(8)	111.0(11)		

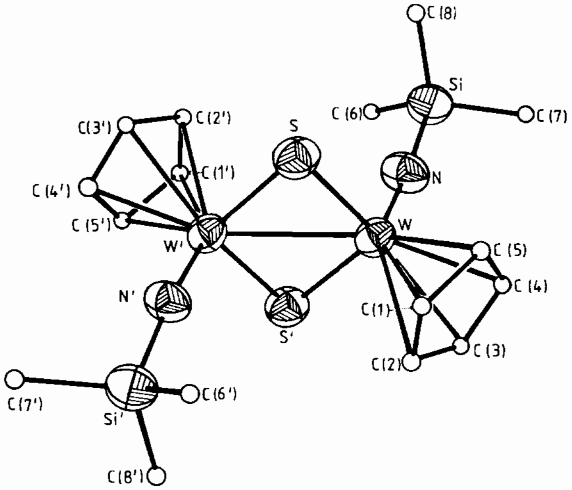
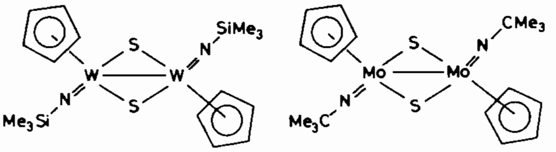


Fig. 1. Molecular structure of $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**).

The structure analysis confirms that the binuclear molecule **1** has the centrosymmetric structure A with a planar $W_2(\mu\text{-}S)_2$ unit. Both the distance between the two tungsten atoms (2.903(3) Å) and the acute angle at the two sulfur bridges (77.0(1)°) are consistent with the formulation of a W–W single bond. The terminal $NSiMe_3$ groups are coordinated in a nearly linear mode (angle WNSi 170.9(25)°), as expected for 4-electron type ligands.

The geometry of the ditungsten complex **1** is very similar to that of the dimolybdenum complex $Cp_2Mo_2(\mu\text{-}S)_2(N^tBu)_2$, described by Dahl and coworkers [11] in 1974. Table IV summarizes the most important distances and angles for the two compounds. Marginal differences may be seen in the fact that the central $M_2(\mu\text{-}S)_2$ core is slightly more compact in **1** and that the $NSiMe_3$ ligand in **1** is attached in a

TABLE IV Comparison of Structural Data for $Cp_2W_2(\mu\text{-}S)_2(NSiMe_3)_2$ (**1**) and $Cp_2Mo_2(\mu\text{-}S)_2(NCMe_3)_2$ [11]



W–W	2.903(3) Å	Mo–Mo	2.920(1) Å
W–S	2.334(3); 2.330(7) Å	Mo–S	2.343(1); 2.340(1) Å
W–N	1.743(8) Å	Mo–N	1.733(4) Å
N–Si	1.735(9) Å	N–C	1.440(6) Å
angle SWS	103.0(3)°	angle SMoS	102.86(4)°
angle WSW	77.0(1)°	angle MoSMo	77.14(4)°
angle WNSi	170.9(25)°	angle MoNC	176.3(3)°
S•••S	3.651(7) Å	S•••S	3.661(2) Å

slightly more bent mode (angle WNSi 170.9(25)°) than the N^tBu ligand (angle MoNC 176.3(3)°) in Cp_2-$Mo_2(\mu\text{-}S)_2(N^tBu)_2$. These effects are significant only within 1σ, however.

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