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SOLID STATE STRUCTURE AND REACTIVITY IN SOLUTION. THE CRYSTAL AND MOLECULAR STRUCTURES OF $(OC)_4W(t\text{-}BuS(CH_2)_nS\text{-}t\text{-}Bu)$ ($n = 3, 2$)

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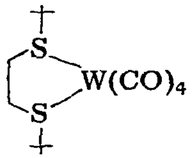
Summary

The crystal and molecular structures of the compounds having composition $(OC)_4W(t\text{-}BuS(CH_2)_nS\text{-}t\text{-}Bu)$ ($n = 3,2$) were determined from single crystal X-ray diffraction data collected with a computer controlled diffractometer, using Mo-K_α radiation. The data that follow are given in the order $n = 3$ first, followed by the relevant data for the derivative with $n = 2$. Space group, $P2_12_12_1$ and cell constants: a 9.388(4), b 9.548(2), c 21.989(11) Å; D(calc) 1.74 g cm^{-3} and Z 4 molecules per unit cell. Space group $C2/c$ and cell constants: a 25.568(9), b 8.958(3), c 16.457(2) Å and β 95.810(13)°; D(calc) 1.78 g cm^{-3} and Z 8 molecules per unit cell. Both structures were solved by Patterson methods using data corrected for absorption. Final refinements converged to $R(F)$ factors of 4.6 and 6.3%, respectively, for ($n = 3$ and 2). The W—S distances when $n = 3$ are 2.574(5) and 2.582(5) Å, the S—W—S angle is 79.1(1)° and the non-bonded S···S is 3.284(7) Å. When $n = 2$, W—S distances are 2.559(5) and 2.565(4) Å, the S—W—S angle is 80.8(1)° and the non-bonded S···S distance is 3.323(6) Å. Both molecules contain octahedrally distorted WC_4S_2 fragments which are quite similar in their geometrical details. The overall WC_4S_2 fragments are normal and their structural characteristics compare well with established values.

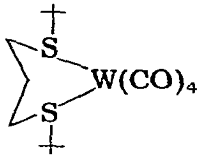
Comparisons between the structural data and reactivity via ligand exchange (replacement of the bidentate ligand) suggest that observed small but statistically significant differences in molecular geometries for the two complexes exert an appreciable cumulative effect upon reactivity.

Introduction

Studies of the kinetics and mechanism of ligand-exchange reactions of (2,2,8,8-tetramethyl-3,7-dithianonane)tetracarbonyltungsten(0) (= (DTN)W(CO)$_4$, I) and (2,2,7,7-tetramethyl-3,6-dithiaoctane)tetracarbonyltungsten(0) (= (DTO)W(CO)$_4$, II); [I and II are (S$_2$)W(CO)$_4$] with phosphines and phosphites (L)



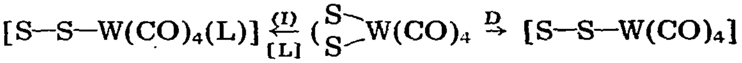
(II)



(I)

$$(S_2)W(CO)_4 + 2\ L \rightarrow L_2W(CO)_4 + S_2 \qquad (1)$$

have shown the initial steps, those involving the substrates, to require chelate ring-opening (D) [1] process and, in some instances, a concurrent attack by L at the substrate with (probably concerted, I [1]) ring-opening [2—6].



$$[S\text{—}S\text{—}W(CO)_4(L)] \underset{[L]}{\overset{(I)}{\leftarrow}} (\begin{smallmatrix}S\\S\end{smallmatrix}\!\!>W(CO)_4 \xrightarrow{D} [S\text{—}S\text{—}W(CO)_4] \qquad (2)$$

Consistent with the often-noted greater "stability" of five- vs. six-membered chelate rings [7], the rates for each process differ significantly for the two substrates (ca. 50-fold faster for the (DTN)W(CO)$_4$ complex). The possibility that structural differences between the two substrates might exist was also suggested by significant differences in their carbonyl-stretching frequencies [(DTO)W(CO)$_4$: 2019m, 1906vs, 1889vs, 1869s [2]; (DTN)W(CO)$_4$: 2019w, 1902vs, 1883s, 1848s cm^{-1} [3] in CHCl$_3$]. Changes in carbonyl-stretching frequencies and force constants have been correlated to bonding and reactivity patterns in a variety of octahedral metal carbonyl complexes [8]. The question is whether or not there exists a difference in the ground states of I and II which could result in changes of molecular parameters and, thus, be detectable by an X-ray study. Also, whether the structural differences, if any, are compatible with the differences already reported [4,5] in the kinetic studies. An interesting case is the comparison by Korvenranta and Saarinen [10] of the structural parameters of 1-nitroso-2-naphthol, 2-nitroso-1-naphthol in their Ni^{2+} and Cu^{2+} derivatives for which the structural parameters of the complexes are essentially identical but their visible, near ultraviolet and infrared absorption spectra and stability in solution are markedly different. Thus, despite recent studies which have indicated that significant differences in substrate reactivities and in their spectroscopic properties may not be reflected strongly in molecular structure [9,10], these two complexes offered the opportunity to study possible changes in molecular geometry as a function of chelate ring size, and their relationship to substrate reactivity.

Experimental

The crystal used for the study of (CO)$_4$W(t-BuS(CH$_2$)$_3$S-t-Bu) was prismatic and had well developed faces. These were easily identified and the distances between them were measured as follows: between (001) and (00$\bar{1}$) 0.009 cm;

$(\bar{2}01)$ and $(20\bar{1})$ 0.016 cm; (201) and $(\bar{2}0\bar{1})$ 0.015 cm; (010) and $(0\bar{1}0)$ 0.027 cm. For compound $(CO)_4W(t\text{-}BuS(CH_2)_2S\text{-}t\text{-}Bu)$, the faces defining the crystal and the distances between them were: (100) and $(\bar{1}00)$ 0.008 cm; $(01\bar{1})$ and $(0\bar{1}1)$ 0.018 cm; (001) and $(00\bar{1})$ 0.026 cm; (010) and $(0\bar{1}0)$ 0.028 cm.

Since data collection for both samples involved similar procedures, we will describe it in full only for the first compound I and give only those details of data collection for II which differed from that procedure.

The crystal of I selected for data collection was mounted approximately along its [010] direction on a X—Y—Z translation head and onto an Enraf—Nonius, computer-controlled CAD-4 diffractometer. All of the diffractometer routines hereafter mentioned can be found in the Enraf—Nonius [11] manual by the interested reader. Throughout, Mo-K_α radiation was used in conjunction with a dense graphite monochromator crystal, assumed to have a parallel arrangement and to be ideally imperfect, whose take-off angle was set at 5.85°, and a counting chain whose discriminator and pulse-height analyzer were set to receive 90% of the incoming beam. The instrument is equipped with attenuators, whose attenuation factors were checked using the diffracted beams from a standard crystal (ammonium rubidium tartrate), provided by the Enraf—Nonius Laboratories. The computer is programmed to assume that diffracted beams exceeding 50000 cps are to be attenuated. Suitably coded information is entered on the magnetic tape output. The crystals are centered automatically using routines, SEARCH, INDEX and DETCELL [11]. The teletype output then gives (a) an orientation matrix, (b) the Niggli matrix [12] and (c) a set of cell constants. The Niggli matrix is used in our laboratory in conjunction with the tables provided by Roof [13] to determine the crystal system and lattice symbol. Once this information is available, the details of the space group symbol are determined by searching for suitable absences by using option MODE = —1 in DATCOL [11]. To obtain strong, high angle reflections for the accurate cell constants determination, the instrument was programmed to collect data in the range of $28° \leqslant 2\,\theta \leqslant 35°$, using a fast pre-scan to estimate whether the reflection would have 400 counts above background. If not, the reflection was considered absent. 30 strong reflections well distributed over reciprocal space were then selected for the determination of the cell constants. The instrument was programmed to center these, and the set was used in conjunction with program PARAM of the X-RAY-72 System [14] to obtain the cell constants listed in Table 1, which also lists other crystallographic parameters used in this study.

The diffracted intensities were collected using the θ—$2\,\theta$ scan technique. The scan speed for I was decided by a pre-scan of about 5 deg./min in which, if the reflection had more than 35 net counts above background, the reflection was deemed observed and re-scanned at a rate such that a minimum of 2000 counts above background were achieved. The maximum time allowed was 570 seconds. For compound II, a reflection was deemed observed if it had more than 70 net counts above background. It was then re-scanned at a rate such that a minimum of 2000 counts above background was achieved. The maximum time allowed was 400 seconds. Backgrounds were measured for 25% of the total scan time on either side of the peak, and for any measured reflection the width of the scan was calculated by the equation scan range = $A + B \tan\theta$ with A 1.00° and B 0.40° for I and A 0.90° and B 0.35° for II. The settings of the variable aperture

TABLE 1

CRYSTAL DATA

	Compound I	Compound II
Empirical formula	$C_{15}H_{24}O_4S_2W$	$C_{14}H_{22}O_4S_2W$
Molecular weight	516.32 g mol^{-1}	502.30 g mol^{-1}
Space group	$P2_12_12_1$	$C2/c$
Cell constants	a 9.388(4) Å b 9.548(2) Å c 21.989(11) Å	a 25.568(9) Å b 8.958(3) Å c 16.457(2) Å β 95.810(13)°
Volume	1971.0 Å^3	3750.1 Å^3
Cell contents	Z 4 molecules per unit cell	Z 8 molecules per unit cell
Density (calc.)	1.74 g cm^{-3}	1.78 g cm^{-3}
Absorption coeff.	μ 64.28 cm^{-1}	μ 67.59 cm^{-1}
Crystal orientation	[010] approx.	[203] approx.
Radiation used	Mo-K_α (0.71069 Å)	same
Number of contributing reflections used in final least squares	2829	3677
Number of variables	198	189
Final $R(F)$	4.6%	6.3%

were determined in the same fashion and A and B were set at 5.20 and 2.11 mm, respectively. The crystal-to-source and crystal-to-detector distances were fixed at 216 and 173 mm, respectively. In order to test the reliability of the electronics and the stability of the crystal, 3 reflections (2,4,4; 3,4,8 and 2,2,10) were used to monitor intensity every 70 reflections. For compound II, two reflections (0,6,2 and 10,2,2) were measured every 30 reflections. No significant variations in the standards were detected. The decollation of the data was done using a locally written program.

A total of 4027 independent reflections were collected for I in the range of $4.0° \leqslant 2\,\theta \leqslant 65.0°$. 2332 reflections were classified as "observed", with the remaining being termed "less-thans". A total of 5131 reflections were collected for II in the range of $6.0° \leqslant 2\,\theta \leqslant 60.0°$ and 2394 reflections were classified "observed". Standard deviations in the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{\text{Tot}} + 2\,\Sigma I_{\text{BG}}$. Lorentz and polarization factors were applied in converting the intensities to structure factors amplitudes, $|F_0|$. Absorption corrections were done for both compounds. The transmission coefficients found for I and II ranged between 0.47 to 0.64 and 0.33 to 0.58, respectively. Standard deviations in the structure amplitudes $\sigma(|F_0|)$, were estimated as $\sigma(|F_0|) = \sigma(I)/2\,L_p|F_0|$. The polarization expression used for crystal monochromatized radiation was that given by Kerr and Ashmore [35].

Solution and refinement

The X-Ray '72 System [14] was used in data reduction and refinement. Both structures were solved by Patterson methods. A three dimensional Patterson map was computed for both compounds and the positions of the tungsten atoms were determined. All the remaining non-hydrogen atoms were easily found from successive difference Fourier maps and refined. Conversion to anisotropic thermal parameters was then accomplished.

Hydrogen atoms were added at theoretically calculated positions (C—H 0.95 Å) but were not refined. In the final cycle of full matrix least squares for I, 2829 reflections were used (2332, "observed" and 497 "less-thans" for which $|F_c| > |F_0|$). For II, 3677 reflections were used (2394 "observed" and 1283 "less-thans"). The refinement converged to the following final unweighted and weighted agreement factors

$$R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.046$$

$$R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.049$$

for compound I and 0.063 and 0.067 for compound II. The function minimized during all least squares refinements was $\Sigma w(|F_0| - |F_c|)^2$ where w, the weighting factors, were $\sigma(|F_0|)^{-2}$. The atomic scattering curves of Cromer and Mann [15] were used for the non-hydrogen atoms and for hydrogen the curve of Stewart et al. [16] was used. Corrections for the real and imaginary parts of the anomalous dispersion for W and S were also applied [17]. The estimated standard deviations were computed from the inverse matrix of the final full matrix least squares cycle. Final positional and thermal parameters for compound I are presented in

(continued on p. 31)

TABLE 2

FINAL POSITIONAL PARAMETERS FOR COMPOUND I

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
W	0.22693(7) [a]	0.00210(11)	0.10964(3)	H1	0.0808	−0.2508	−0.0476
S1	0.2364(5)	−0.0992(5)	0.0008(2)	H2	0.1050	−0.1937	0.0112
S2	0.2738(6)	−0.2583(5)	0.1323(2)	H3	0.8130	−0.4405	0.0142
C1	0.0959(26)	−0.2298(23)	−0.0059(12)	H4	0.2364	−0.3856	0.0194
C2	0.1394(29)	−0.3660(24)	0.0285(10)	H5	0.0364	−0.3106	0.1083
C3	0.1231(26)	−0.3569(21)	0.0988(12)	H6	0.1216	−0.4489	0.1153
C4	0.4448(26)	0.0452(26)	0.1066(12)	H7	0.3923	−0.1327	0.2370
C5	0.0133(24)	−0.0148(45)	0.1148(12)	H8	0.4011	−0.2563	0.2835
C6	0.2019(34)	0.2063(32)	0.0755(14)	H9	0.4875	−0.2613	0.2227
C7	0.2233(28)	0.0765(31)	0.1953(12)	H10	0.0511	−0.3102	0.2211
C8	0.2720(30)	−0.3084(28)	0.2151(11)	H11	0.1142	−0.1650	0.2378
C9	0.4020(31)	−0.2311(35)	0.2417(12)	H12	0.1251	−0.2887	0.2837
C10	0.1260(36)	−0.2634(39)	0.2419(14)	H13	0.2127	−0.5219	0.1918
C11	0.2897(31)	−0.4797(32)	0.2129(12)	H14	0.2888	−0.5049	0.2547
C12	0.1833(24)	0.0235(25)	−0.0608(10)	H15	0.3770	−0.5057	0.1942
C13	0.1971(33)	−0.0464(31)	−0.1244(11)	H16	0.1373	−0.1266	−0.1258
C14	0.0338(26)	0.0803(29)	−0.0499(13)	H17	0.1699	0.0163	−0.1559
C15	0.2972(28)	0.1388(31)	−0.0583(12)	H18	0.2932	−0.0740	−0.1305
O1	0.5628(19)	0.0611(23)	0.110(12)	H19	−0.0315	0.0043	−0.0488
O2	−0.1091(18)	−0.0192(37)	0.1215(10)	H20	0.0318	0.1284	−0.0121
O3	0.1751(26)	0.3163(19)	0.0737(11)	H21	0.0067	0.1429	−0.0814
O4	0.2280(29)	0.1296(25)	0.2419(9)	H22	0.2701	0.2015	−0.0898
				H23	0.3892	0.1012	−0.0657
				H24	0.2965	0.1845	−0.0199

[a] Numbers in parentheses in this and succeeding tables are the estimated standard deviations in the least significant digits.

TABLE 3

FINAL ANISOTROPIC THERMAL PARAMETERS FOR THE NON HYDROGEN ATOMS OF COMPOUND I ($\times 10^3$) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	37.5(2)	35.1(2)	43.3(3)	2.4(6)	—4.1(3)	—0.6(6)
S1	36(2)	40(2)	48(2)	2(2)	—10(2)	0(2)
S2	43(2)	42(2)	48(2)	4(2)	—3(2)	10(2)
C1	66(14)	40(11)	74(15)	—10(11)	—36(13)	6(11)
C2	82(17)	52(12)	44(11)	9(13)	—10(12)	—17(10)
C3	61(14)	35(9)	89(18)	—24(10)	—13(13)	13(11)
C4	60(14)	69(15)	57(13)	—5(11)	—14(12)	—6(13)
C5	48(12)	145(22)	71(15)	—11(21)	3(11)	—64(22)
C6	83(21)	80(19)	111(22)	10(17)	—33(18)	—55(17)
C7	42(12)	118(19)	66(16)	24(15)	—3(14)	—1(15)
C8	60(14)	74(15)	59(14)	4(14)	—12(13)	8(12)
C9	85(19)	90(21)	52(14)	13(18)	—27(14)	—7(15)
C10	100(23)	96(23)	74(20)	20(20)	41(18)	15(19)
C11	114(18)	57(17)	84(16)	21(20)	8(15)	15(15)
C12	61(12)	51(15)	55(11)	—5(11)	2(10)	7(11)
C13	100(21)	95(22)	57(14)	14(17)	—18(14)	—8(14)
C14	49(13)	73(16)	87(19)	21(12)	—7(13)	10(15)
C15	60(16)	106(21)	77(16)	—11(15)	—4(13)	66(16)
O1	40(10)	112(17)	148(18)	—14(10)	—7(12)	—19(16)
O2	43(10)	185(20)	149(17)	—10(20)	11(11)	5(26)
O3	105(17)	38(9)	134(19)	13(11)	—11(16)	7(11)
O4	121(19)	128(18)	71(12)	9(18)	—4(14)	—43(13)

[a] The form of the anisotropic thermal ellipsoid is

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

and

$$\beta_{ij} = 2\pi^2 / U_{ij} a_i^* a_j^* \ (\text{Å})^2$$

TABLE 4

FINAL POSITIONAL PARAMETERS FOR THE ATOMS OF COMPOUND II

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
W	0.11119(3)	—0.22673(9)	0.12402(4)	H1	0.1450	—0.0261	—0.0521
S1	0.0739(1)	—0.1727(6)	—0.0236(2)	H2	0.0941	0.0345	—0.1001
S2	0.1303(2)	0.0535(6)	0.1196(2)	H3	0.0668	0.1348	0.0232
C1	0.1089(7)	—0.0039(27)	—0.0490(9)	H4	0.1206	0.2039	0.0080
C2	0.1031(8)	0.1148(24)	0.0211(11)	H5	0.1806	0.3286	0.0888
C3	0.0897(9)	—0.4397(28)	0.1286(10)	H6	0.1805	0.3190	0.1829
C4	0.1343(6)	—0.2391(24)	0.2447(14)	H7	0.2334	0.3181	0.1441
C5	0.1803(9)	—0.2929(36)	0.0976(18)	H8	0.2263	—0.0366	0.0529
C6	0.0366(9)	—0.1783(44)	0.1429(18)	H9	0.2104	0.1142	0.0111
C7	0.1961(6)	0.110(24)	0.1319(10)	H10	0.2628	0.1000	0.0657
C8	0.1977(7)	0.2869(26)	0.1374(15)	H11	0.2038	0.0831	0.2523
C9	0.2273(6)	0.0688(25)	0.0590(13)	H12	0.2196	—0.0573	0.2053
C10	0.2213(8)	0.0486(27)	0.2076(13)	H13	0.2570	0.0797	0.2143
C11	0.0907(7)	—0.3027(30)	—0.1043(11)	H14	0.0208	—0.2460	—0.1758
C12	0.0573(16)	—0.2425(42)	—0.1821(12)	H15	0.0670	—0.1430	—0.1939
C13	0.0612(10)	—0.4408(41)	—0.0879(20)	H16	0.0660	—0.3093	—0.2235
C14	0.1468(7)	—0.3264(40)	—0.1075(14)	H17	0.0723	—0.4793	—0.0352
O1	0.0760(6)	—0.5664(21)	0.1290(10)	H18	0.0244	—0.4223	—0.0922
O2	0.1472(5)	—0.2471(20)	0.3118(6)	H19	0.0698	—0.5076	—0.1294
O3	0.2218(7)	—0.3455(25)	0.0965(11)	H20	0.1625	—0.2326	—0.1166
O4	—0.0061(7)	—0.1676(40)	0.1615(13)	H21	0.1610	—0.3652	—0.0562
				H22	0.1554	—0.3932	—0.1498

TABLE 5. FINAL ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS OF COMPOUND II ($\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	66.1(4)	51.4(4)	51.9(3)	4.8(4)	8.3(2)	4.8(4)
S1	68(2)	66(3)	58(2)	5(2)	5(2)	—4(2)
S2	95(3)	50(3)	54(2)	9(2)	1(2)	—6(2)
C1	117(14)	93(18)	51(10)	—25(14)	—3(10)	19(11)
C2	127(15)	53(13)	83(13)	8(13)	—21(12)	7(11)
C3	131(17)	80(17)	36(8)	24(14)	12(9)	14(10)
C4	75(11)	71(15)	109(16)	11(10)	15(10)	20(14)
C5	56(14)	61(11)	75(12)	1(7)	—13(11)	13(12)
C6	44(11)	139(32)	119(2)	59(19)	30(12)	30(11)
C7	58(10)	81(15)	59(10)	17(10)	0(8)	—19(10)
C8	80(12)	63(15)	152(19)	—8(12)	3(12)	—29(15)
C9	56(10)	73(16)	141(18)	—5(11)	12(11)	32(14)
C10	139(16)	73(17)	105(15)	—36(15)	—16(13)	—2(14)
C11	81(12)	107(20)	70(11)	—4(13)	2(9)	—27(13)
C12	185(31)	229(52)	48(13)	53(35)	—18(18)	—29(24)
C13	150(22)	122(30)	207(33)	—24(22)	22(21)	—77(27)
C14	85(13)	180(33)	118(17)	16(18)	27(11)	—40(20)
O1	144(13)	68(12)	127(12)	3(11)	36(9)	24(11)
O2	130(10)	148(17)	41(6)	21(11)	7(6)	28(9)
O3	144(17)	106(13)	82(9)	—29(13)	—65(11)	51(9)
O4	97(10)	212(26)	155(15)	27(14)	38(9)	48(17)

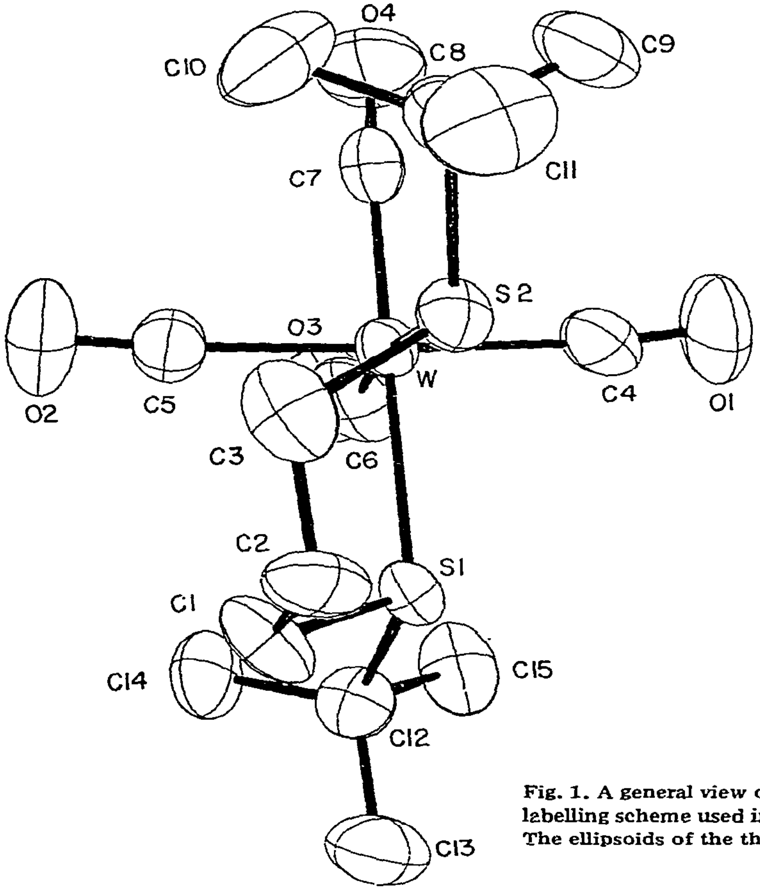


Fig. 1. A general view of compound I showing the labelling scheme used in the crystallographic study. The ellipsoids of the thermal motion are 50% envelopes.

TABLE 6

DISTANCES (Å) AND ANGLES (°) IN COMPOUND I. ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

A. Distances (Å)				B. Angles (°)			
W-S1	2.582(5)	C1—C2	1.569(33)	S1—W—S2	79.1(0.1)	C14—C12—C13	111.8(2.1)
W—S2	2.574(5)	C2—C3	1.556(35)	W—S1—C1	107.9(0.8)	C15—C12—C13	106.4(2.0)
W—C4	2.088(24)	C8—C9	1.541(40)	W—S1—C12	115.5(0.7)	C14—C12—C15	112.4(2.1)
W—C5	2.015(22)	C8—C10	1.553(43)	S1—C1—C2	110.0(1.7)	C4—W—S1	90.6(0.7)
W—C6	2.103(31)	C8—C11	1.644(40)	C1—C2—C3	114.2(1.9)	C4—W—S2	91.7(0.7)
W—C7	2.013(27)	C12—C13	1.554(34)	C2—C3—C2	110.4(1.7)	C4—W—C5	173.1(1.4)
S1—C1	1.820(24)	C12—C14	1.523(33)	C3—S2—W	106.5(0.7)	C4—W—C6	85.1(1.1)
S1—C12	1.860(23)	C12—C15	1.536(36)	W—S2—C8	115.5(0.8)	C4—W—C7	88.7(1.0)
S2—C3	1.852(24)	S1—S2	3.284(7)	C3—S2—C8	104.4(1.2)	C5—W—S1	93.2(0.8)
S2—C8	1.883(24)	S2—C7	3.516(29)	S2—C8—C9	103.8(1.7)	C5—W—S2	94.7(1.2)
C4—O1	1.121(30)	S1—C6	3.363(31)	S2—C8—C11	102.9(1.6)	C5—W—C6	89.0(1.5)
C5—O2	1.160(28)	C6—C7	2.919(41)	S2—C8—C10	107.7(1.9)	C5—W—C7	87.6(1.1)
C6—O3	1.080(36)			C9—C8—C10	115.0(2.3)	C6—W—S1	91.2(0.9)
C7—O4	1.144(34)			C10—C8—C11	112.0(2.3)	C6—W—S2	169.8(0.9)
				C9—C8—C11	114.1(2.3)	C6—W—C7	90.3(1.2)
				C1—S1—C12	100.2(1.1)	C7—W—S1	178.3(0.8)
				S1—C12—C14	110.9(1.6)	C7—W—S2	99.4(0.8)
				S1—C12—C15	103.8(1.6)	W—C4—O1	173.2(2.4)
				S1—C12—C13	112.2(1.7)	W—C5—O2	175.2(2.7)
						W—C6—O3	163.1(3.0)
						W—C7—O4	173.5(2.5)

TABLE 7

DISTANCES (Å) AND ANGLES (°) IN COMPOUND II. ESTIMATED STANDARD DEVIATIONS IN PARENTHESES.

A. Distances (Å)		B. Angles (°)			
W—S1	2.565(4)	S1—W—S2	80.8(0.1)	C5—W—S1	96.0(0.8)
W—S2	2.559(5)	W—S1—C1	103.3(0.5)	C5—W—S2	96.5(0.9)
W—C3	1.988(25)	W—S1—C11	118.0(7)	C5—W—C6	173.3(1.3)
W—C4	2.017(22)	S1—C1—C2	107.7(1.2)	C5—W—C3	88.6(1.1)
W—C5	1.954(25)	C1—C2—S2	113.4(1.4)	C5—W—C4	91.2(1.0)
W—C6	2.011(26)	C2—S2—W	105.7(0.7)	C6—W—S1	80.7(0.8)
S1—C1	1.827(23)	W—S2—C7	117.9(0.7)	C6—W—S2	88.8(1.1)
S1—C11	1.848(22)	C2—S2—C7	107.2(0.9)	C6—W—C3	86.1(1.3)
S2—C2	1.785(19)	S2—C7—C8	108.6(1.2)	C6—W—C4	92.7(1.0)
S2—C7	1.752(16)	S2—C7—C10	108.8(1.4)	C3—W—S1	98.0(0.5)
C3—O1	1.188(31)	S2—C7—C9	113.6(1.2)	C3—W—S2	174.9(0.7)
C4—O2	1.122(24)	C8—C7—C9	106.0(1.6)	C3—W—C4	87.9(0.8)
C5—O3	1.162(31)	C9—C7—C10	110.6(1.6)	C4—W—S1	170.7(0.6)
C6—O4	1.167(32)	C8—C7—C10	109.1(1.6)	C4—W—S2	92.6(0.6)
C1—C2	1.587(28)	C1—S1—C11	101.6(1.0)	W—C3—O1	177.9(1.5)
C7—C8	1.579(32)	S1—C11—C13	103.6(1.7)	W—C4—O2	179.5(2.0)
C7—C9	1.550(27)	S1—C11—C14	114.8(1.6)	W—C5—O3	166.8(2.5)
C7—C10	1.455(27)	S1—C11—C12	102.9(1.8)	W—C6—O4	170.2(3.2)
C11—C12	1.561(33)	C13—C11—C12	101.0(2.1)		
C11—C13	1.487(42)	C14—C11—C12	118.6(2.1)		
C11—C14	1.457(27)	C13—C11—C14	113.8(2.4)		
S1—S2	3.323(6)				
S2—C4	3.329(23)				
S1—C3	3.459(21)				
C3—C4	2.780(30)				

Tables 2 and 3 and for compound II in Tables 4 and 5. Interatomic distances and angles are given in Table 6 for compound I and in Table 7 for compound II. The equations of the least squares planes through selected groups of atoms are given in Table 8. The stereo drawings for compound I (Fig. 1, 2, 3) and for compound

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TABLE 8

LEAST SQUARES PLANES [a] THROUGH SELECTED GROUPS OF ATOMS AND DEVIATIONS OF ATOMS FROM THESE PLANES (in Å)

Compound I				Compound II			
A Plane through S1, S2, C6 and C7				*A Plane through S1, S2, C3 and C4*			
$0.9893\,x + 0.1431\,y - 0.0287\,z = 2.0831$				$0.9356\,x - 0.2321\,y - 0.2661\,z = 2.2815$			
S1	−0.024	C6	0.027	S1	−0.015	C3	0.018
S2	0.023	C7	0.026	S2	0.016	C4	−0.019
W	−0.041	C5	−2.051	W	0.116	C5	2.063
C4	2.043			C6	−1.881		
B Plane through W, S1, C2, and C3				*B Plane through W, S1, S2 and C2*			
$0.9471\,x - 0.2891\,y + 0.1394\,z = 2.3613$				$0.9303\,x - 0.1706\,y - 0.3246\,z = 2.1630$			
W	−0.013	C2	−0.025	W	−0.023	S2	0.033
S1	0.016	C3	0.021	S1	0.020	C2	−0.030
S2	1.191	C1	−0.893	C1	0.771		

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[a] Planes are expressed as $px + qx + rz = s$ in orthogonal (Å) space.

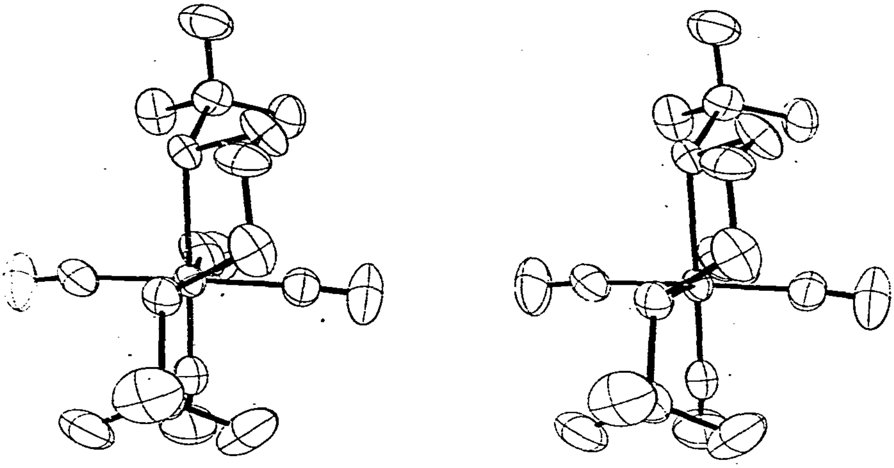

Fig. 2. A stereoscopic view of molecule I.

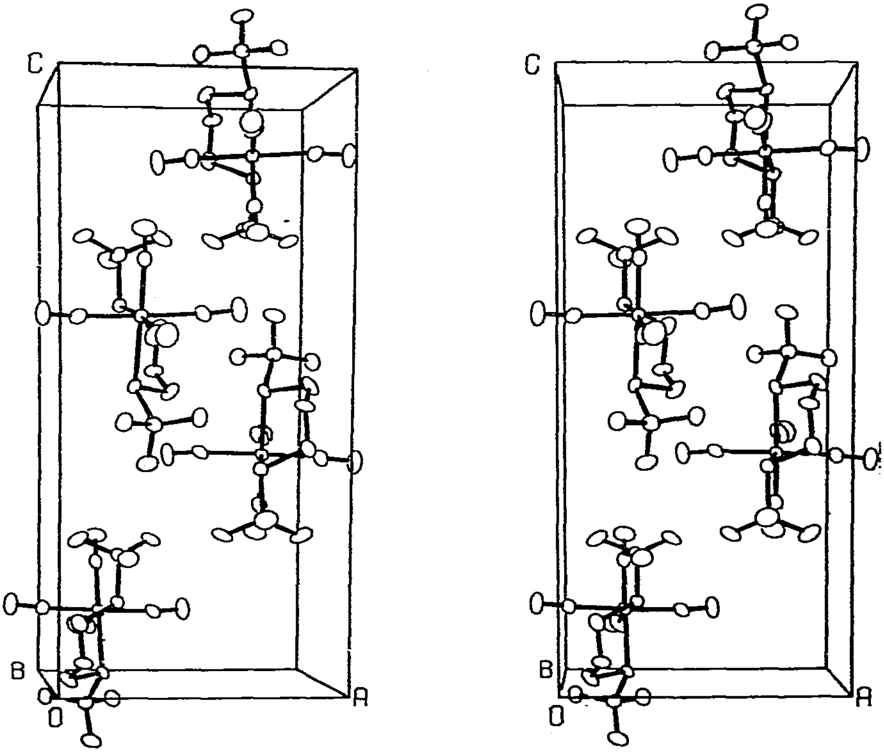

Fig. 3. A packing diagram of compound I.

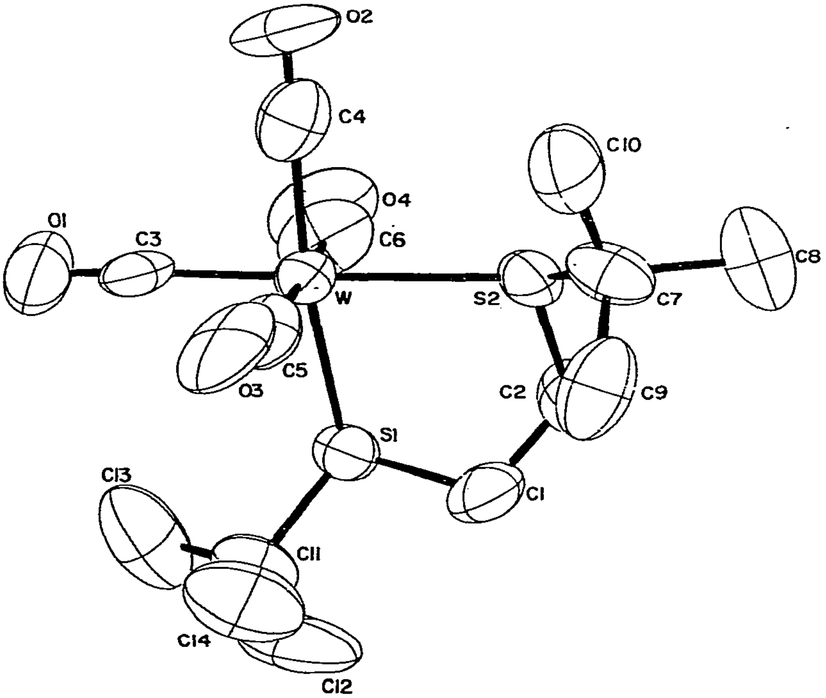

Fig. 4. A general view of compound II showing the labelling scheme used in the crystallographic study. The ellipsoids of the thermal motion are 50% envelopes.

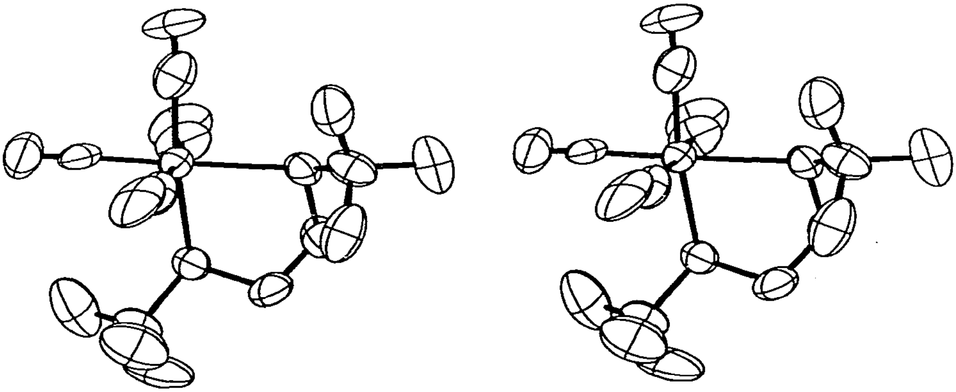

Fig. 5. A stereoscopic view of molecule II.

II (Fig. 4, 5, 6) were obtained by using Johnson's ORTEP 2 [18]. Final observed and calculated structure factors are available *.

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* A table of Structure Factors has been deposited as NAPS document No. 03310 (66 pages) with ASIS/NAPS, c/o Microfische Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017. A copy may be secured by citing the document number and remitting $ 3.00 for microfiche and $ 16.50 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications. Outside the U.S.A. or Canada, postage is $ 3.00 for a photocopy or $ 1.00 for a fiche.

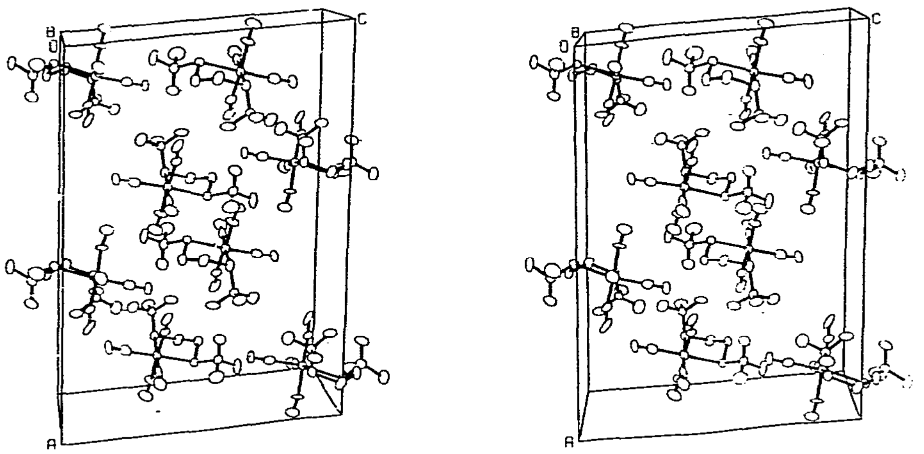

Fig. 6. A packing diagram of compound II.

Description of the structure and discussion

The configuration around the central W atom can be best described as a distorted octahedron, the equatorial plane being formed by 2 carbonyls and 2 sulfur atoms. The deviation of the W atom from the equatorial plane is 0.041 Å for compound I and 0.116 Å for compound II. A deviation of 0.06 Å of the W atom from an equatorial plane formed by 4 carbonyls was found by Cannas et al. [22].

Table 9 was prepared in order to compare our current results with values given in the literature. The various examples listed in this table have a central W atom bonded to sulfur and to various other ligands such as (π-C_5H_5) or carbonyls. The geometry around the W atom found for I and II can be best compared to various other octahedral configurations [19—22], where the equatorial plane is formed by 2 carbonyl groups and 2 sulfur atoms [19] or by 4 carbonyl ligands [20—22].

The distortion from the theoretical octahedral geometry around the W atom is caused by the fact that the six ligands are different and the W—ligand distances vary. Thus, the W—S distances for I and II are 2.582(5), 2.574(5) and 2.565(4), 2.559(5) Å, respectively, whereas the average W—C(0) distance is 2.02 Å.

The W—S distances found for I and II are similar to those observed by others [19,20—22,24,26]. An interesting case is that of $(\pi\text{-}C_5H_5)_2W(SC_6H_5)_2M(CO)_4$ [19] where M = Cr, Mo or W. The W—S bonds in the $(\pi\text{-}C_5H_5)_2W(SC_6H_5)_2$ fragment are in all three cases significantly shorter than the corresponding distances in $(CO)_4W(SC_6H_5)_2$. This decrease in the W—S distance when going from carbonyl ligands to (π-C_5H_5) was observed also in other compounds [23,27] and reflects the better ability of the sulfur atom to compete for the W electrons in S_2W-$(\pi\text{-}C_5H_5)_2$ than in compounds which contain carbonyl ligands.

The W—C(0) bonds vary in the literature from 1.92 [24] to 2.08 Å [21]. A "*trans*" effect of shortening of the W—C(0) distance for the carbonyl which is opposite the sulfur was observed in some cases [20—22]. The values of the W—C(0) bonds obtained for compounds I and II are thus similar to those found in literature, although a "*trans*" effect was not observed.

The C—S bond lengths found in this study can be best compared to the values of 1.807(16) and 1.819(15) Å observed by Cannas et al. [21] or to those obtained by Elder and Hall [24], although their high estimated standard deviations of 0.04 Å make comparisons difficult. The values of the S—C(ring) bond lengths found for compounds I and II, 1.820(24), 1.852(24) and 1.828(23), 1.785(19) Å, respectively, thus, compare well with values in the literature. The deviations of about 3 σ of some of the S—C(t-Bu) distances observed for I and II [i.e., 1.883(24) and 1.752(16) Å] from the expected value of about 1.81 Å are probably not significant.

Deviation from a regular octahedral environment is greatest for the S—W—S angle where a contraction from 90° to 79.1 (I) and 80.8° (II) occurs. This contraction of the S—W—S angle is similar to those found by others [19b,23—25] where the S—W—S fragments are part of 5-membered rings of the type WS_2C_2. The S—W—S angle was found to be even smaller in the four-membered WS_2M ring [19] (which has no W—M bond) where M = Cr, Mo or W. This contraction of the S—W—S angle is accompanied by an increase in both S—W—C_{eq}(*cis*) angles to 101° and a corresponding decrease in both S—W—C_{eq}(*trans*) angles to 170 and 169°. The higher S—W—S angles observed in this study (79.1 (I) and 80.8° (II)) are accompanied by an increase in only one of the S—W—C_{eq}(*cis*) angles to 99.4 (I) and 98.0° (II), while the other remains close to 90° (i.e., 91.2 and 92.6°, respectively). As expected, there is also a corresponding decrease in only one of the two S—W—C_{eq}(*trans*) angles to 169.8 (I) and 170.7° (II) while the other remains largely undisturbed with values of 178.3 and 174.9°, respectively. A somewhat similar behavior was found by Davis and Kilbourn for $(\pi\text{-}C_5H_5)_2TiS_2(CH_3)_2Mo(CO)_4$ [30]. The configuration around the Mo atom is octahedral. The S—Mo—S angle is 94.6° and this increase is accompanied by a corresponding decrease in only one of the S—Mo—C_{eq}(*cis*) angles to 85.3° while the other angle remains largely undisturbed with a value of 89.3°. A similar but smaller distortion was found also by Bennett et al. [34] for a $(CO)_4CrP_2$ octahedron. The possibility that this type of distortion is dependent upon the identity of the metal atom is under investigation. The C_{eq}—W—C_{eq} angles found in this study are 90.3 (I) and 87.9° (II) and compare well with the corresponding angles found for $W(CO)_5S$ [20—22] and with the value of 87° found by Prout and Rees [19b]. Thus, the C_{eq}—W—C_{eq} angle remains close to the expected theoretical value and does not vary significantly when changing 2 carbonyls to 2 sulfurs in the equatorial plane. The S—W—C_{axial} and the C_{axial}—W—C_{axial} angles observed in this study are close to those given by Prout and Rees [19b]. The C_{eq}—W—C_{axial} angles compare well with those listed in literature [19b,20—22]. The W—S—C_{ring} angles are close to those found by others [23—25].

The relationship between structure and reactivity

While structural differences in the two substrates are not large, the pattern of statistically-significant differences is reasonably correlated both to the observed reactivity, and to the observed carbonyl stretching frequencies for the two complexes. Differences suggest that "release of strain" which is expected to accompany formation of the transition states for both the dissociative and interchange paths should be more important for $(DTN)W(CO)_4$, although it is also reason-

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Table 9

A Comparison of Molecular parameters with literature values. Distances are in Å and angles in degrees.

Compound	W-S	W-C(O)	C=O	S-C	S-W-S	S-W-C^a_a	S-W-C$^a_{eq}$(trans)	S-W-C$_{eq}$(cis)	C$_{eq}$W-C$_{eq}$	C$_a$-W-C$_a$	C$_a$-W-C$_{eq}$	Ref.
(CO)$_4$W[(Bu^t-S(CH$_2$)$_3$S-Bu^t)]	2.582(5) 2.574(5)	2.09(2) 2.01(2) 2.10(3) 2.01(3)	1.16(3) 1.08(3) 1.14(3) 1.12(3)	1.82(2) 1.86(2) 1.85(2) 1.88(2)	79.1(1)	90.6(7) 91.7(7) 93.2(8) 94.7(1.2)	169.8(9) 178.3(8)	91.2(9) 99.4(8)	90.3(1.2)	173.1(1.4)	85.1(1.1) 88.7(1.0) 89.0(1.5) 87.6(1.1)	This Study
(CO)$_4$W[(Bu^t-S(CH$_2$)$_2$S-Bu^t)]	2.565(4) 2.559(5)	1.99(2) 2.02(2) 1.95(2) 2.01(3)	1.19(3) 1.12(2) 1.16(3) 1.17(3)	1.83(2) 1.85(2) 1.79(2) 1.75(2)	80.8(1)	96.5(9) 96.0(8) 88.8(1.1) 80.7(8)	170.7(6) 174.9(7)	92.6(6) 98.0(5)	87.9(8)	173.3(1.3)	91.2(1.0) 88.6(1.1) 92.7(1.0) 86.1(1.3)	This Study
(π-C$_5$H$_5$)$_2$W(SC$_6$H$_5$)$_2$M(CO)$_4$ M=Cr	2.483(7) 2.491(7)			1.79(3) 1.77(3)	71.7(2)							19
M=Mo	2.526(5) 2.483(6)			1.79(2) 1.81(2)	72.6(2)							
M=W	2.48(1) 2.49(1) 2.57(1) 2.59(1)	1.99(4) 2.06(4) 2.06(4) 2.10(4)	1.09(6) 1.10(6) 1.19(6) 1.09(6)	1.76(3) 1.76(4)	72.8(3) 69.7(3)	89(1) 92(1) 97(1) 96(1)	169(1) 170(1)	101(1) 101(1)	87(1)	171(2)	82(2) 86(2) 91(2) 89(2)	
(CO)$_5$W-($\underline{\text{S=C-NH-CH}_2\text{-CH}_2\text{-S}}$)	2.56(1)	2.02(1) 2.02(1) 2.00(1) 2.06(1) 1.97(1)^b	1.15(2) 1.21(2) 1.14(2) 1.11(2) 1.14(2)	1.81(2) 1.78(2)					90.7(7)^d 92.0(7) 87.9(7) 89.5(7)		86.3(7) 89.8(7) 92.3(7) 89.2(7)	20
(CO)$_5$W-$\underline{\text{S-CH}_2\text{-CH}_2\text{-NH-}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{-CH}_2}$	2.551(14)	2.051(14) 2.080(17) 2.030(13) 2.012(17) 2.000(18)^b	1.087(21) 1.150(18) 1.133(21) 1.160(18) 1.148(21)	1.807(16) 1.819(15)			176.9(6)^c 173.2(5)		89.1(6)^d 92.6(6) 88.0(6) 90.1(6)		88.1(6) 88.4(6) 85.7(6) 89.1(7)	21

$(CO)_5W-(S=\underline{C-NH-CH_2-CH_2-S-CH})_2$	2.556(8)	2.03(3) 2.05(2) 2.04(2) 2.06(2) 1.95(2)^b	1.17(3) 1.15(4) 1.10(3) 1.15(3) 1.11(3)	1.83(3) 1.81(3)			176.2(10)^c 174.6(10)		86.8(10)^d 94.2(10) 88.9(9) 90.0(9)		89.5(11) 88.8(9) 87.3(10) 87.5(9)	22
$(\pi-C_5H_5)_2W(S_2C_6H_4)$	2.421(2)				82.3(3)							23
$(DTH)(CO)_3ClWSnCH_3Cl_2$ $DTH=CH_3SCH_2CH_2SCH_3$	2.537(8) 2.580(8)	1.99(4) 1.92(3) 1.98(3)	1.15(4) 1.16(4) 1.16(4)	1.83(4) 1.87(4) 1.80(4) 1.80(4)	80.6(3)							24
$[(C_6H_5)_4As]_2[W(S_2C_2(CN)_2)_3$	2.383(5) 2.368(5) 2.363(5)			1.73(2) 1.74(2)	82.0(2) 82.1(2)							25
$[N(C_2H_5)_4][(CO)_5W(C_8H_4OS_2F_3)]$	2.543(2)											26
$(\pi-C_5H_5)_2WS_4$	2.420(3) 2.419(3)				89.1(1)							27
$WS_8N_4BrC_{20}H_{40}$	2.524(7) 2.494(11)											28

[a] C_a = axial carbon, C_{eq} = equatorial carbon.

[b] carbonyl trans to sulphur.

[c] C_{eq}-W-C_{eq}(trans) angles.

[d] C_{eq}-W-C_{eq}(cis) angles.

able to expect that other transition state effects may also exert a significant influence on reactivity. The "release of strain" effect is indicated by differences in the internal ring angles, particularly in the S—W—S values. The smaller "bite" in the (DTN)W$(CO)_4$ complex results in a smaller ((3.28 vs. 3.32 Å) non-bonded S—S distance. It is interesting to note in this regard that these distances are substantially less than the expected van der Waals' intermolecular non-bonded distance of 3.7 Å [31]. Branden has reported the structure of 2 $HgCl_2 \cdot SEt_2$, which contains diethyl sulfide coordinated to mercury, and which may be taken as a model for "unstrained" M—S—C angles [32]. The average Hg—S—C angle in that adduct is 103°, which compares closely with the average observed for W—S—C_{ring} in (DTO)W$(CO)_4$ (104.5°), but is significantly smaller than that in (DTN)W$(CO)_4$ (107.4°). These values also support release of strain upon ring-opening in these systems.

The W—S bond lengths in I and II are (2.582(5), 2.574(5) Å vs. 2.565(4), 2.559(5) Å, respectively. The somewhat longer average bond length in (DTN)W$(CO)_4$ is consistent both with greater reactivity via ring-opening in that complex and with the significantly lower carbonyl stretching frequencies observed for normal modes involving carbonyls *trans* to sulfur. In particular, a ca. 20 cm^{-1} difference is noted in the B_2 modes, which involve the antisymmetric stretch of the carbonyls *trans* to sulfur [3,33]. This difference is consistent with weaker W—S π-bonding in the (DTN)W$(CO)_4$ complex, with the observed reactivity and with the longer average bond length. Thus it is reasonable to presume that these small but statistically significant differences in substrate geometry exert a significant cumulative effect upon reactivity.

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