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ORGANOTHIOMETALLATE - ALKYNE ADDITION PRODUCTS. THE CRYSTAL AND
 MOLECULAR STRUCTURE OF $[(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{O})\text{SMe}\}(\text{CO})_2]$

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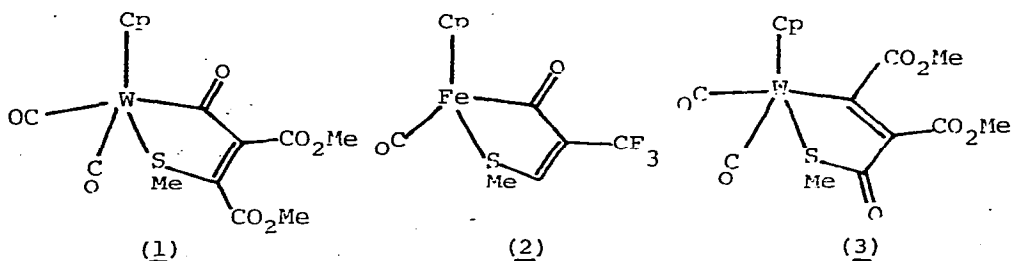
Summary

The title compound is the final product of the reaction between dimethylacetylene dicarboxylate and $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{SMe})(\text{CO})_3]$ 1. Its molecular structure has been established by an X-ray analysis based on 3301 diffractometric intensities. The crystals are monoclinic, space group $P2_1/a$, with four molecules in a cell of dimensions $a = 10.323(2)$, $b = 16.016(2)$, $c = 10.437(2)\text{\AA}$, $\beta = 103.56(2)^\circ$. After least-squares refinement $R = 0.036$. The tungsten co-ordination is square-pyramidal, the apical site being occupied by the centroid of the cyclopentadienyl ring. The basal co-ordination sites contain two carbonyl groups and also the sulphur and σ -bonded carbon atoms of a chelating carbothiolic methyl ester ligand derived from the incoming alkyne and CO and SMe groups of the original complex. The W-S and σ -W-C bond lengths are $2.440(2)$ and $2.194(7)\text{\AA}$.

Introduction

Reactions between alkynes and organothiometallates $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{SMe})(\text{CO})_n]$, ($\text{M} = \text{Mo}, \text{W}, n = 3$; $\text{M} = \text{Fe}, n = 2$) have recently been investigated by Davidson and Shiralian [1] and by Petillon and Sharp [2]. In general, they proceed without loss of carbon monoxide to give products containing structurally novel ligands arising from condensation of the alkyne with the mercapto and carbonyl groups of the parent complex. The nature of the product appears to depend both on the transition metal and on the alkyne. We are at present investigating by diffraction methods the molecular structures of several complexes obtained from such reactions, partly because of their intrinsic interest and partly to facilitate understanding of the chemical processes involved in their formation.

Dimethylacetylene dicarboxylate undergoes an addition reaction with $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{SMe})(\text{CO})_3]$ to give initially a complex formulated as (1) on the basis of spectroscopic evidence [1] and by analogy with (2). The complex (2) is an addition product of $\text{F}_3\text{CC}\equiv\text{CH}$ $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe})(\text{CO})_2]$ and has been characterised both spectroscopically [2] and crystallographically [3]. In solution (1) isomerises to (3). We report here the results of an X-ray crystal structure analysis of (3). An account of the reactions leading to (3) and of related reactions will be given elsewhere [4].



ExperimentalCrystal data

$C_{15}H_{14}O_7$ SW, M.W. 522.2. Monoclinic, space group $P2_1/a$ (C_{2h}^5 -No.14),
 $a = 10.323(2)$, $b = 16.016(2)$, $c = 10.437(2)\text{\AA}$, $\beta = 103.56(2)^\circ$,
 $U = 1677.5\text{\AA}^3$, $Z = 4$, $D_c = 2.068\text{ g cm}^{-3}$, $F(000) = 1000$. Mo- K_α
radiation, $\lambda = 0.71069\text{\AA}$, $\mu(\text{Mo-}K_\alpha) = 71.9\text{ cm}^{-1}$.

Measurements

A crystal of dimensions 0.47 x 0.13 x 0.09 mm was used for all measurements. It was mounted on an Enraf-Nonius CAD-4F diffractometer equipped with a graphite monochromator. The crystal orientation and cell dimensions were determined from the setting angles of 25 reflections with $15 \leq \theta(\text{Mo-}K_\alpha) \leq 18^\circ$. The intensities of all independent reflections with $2 \leq \theta(\text{Mo-}K_\alpha) \leq 30^\circ$ were measured using continuous $\theta/2\theta$ scans of 0.60° in θ , increased by 25% at each end of the scan range to allow for background. Counting continued either until $\sigma(I)/I < 0.03$ or for 60s, whichever was shorter. The measurements for each reflection were repeated until consistent results were obtained. The crystal orientation and the intensities of two reflections were remeasured at intervals of ca. 2 h throughout the experiment. No change in orientation was observed, but the monitored intensities displayed random fluctuations of up to 7% of their mean values.

The integrated intensities and their standard deviations were derived as described previously ($q = 0.04$) [5] and were corrected for Lorentz-polarisation effects but not for absorption or extinction. The analysis was carried out with 3301 reflections for which $I > 3\sigma(I)$.

Structure analysis

All atoms, apart from hydrogen, were located by Patterson and difference Fourier methods. The final positional and thermal

Table 1

Fractional atomic co-ordinates and isotropic vibrational parameters ($\times 10^4$)

Atom	x	y	z	U_{iso}
W	1770 (1)	0828 (1)	2881 (1)	*
S	3209 (2)	0567 (1)	5057 (2)	*
O (1)	-0400 (7)	1022 (4)	4493 (7)	622 (16)
O (2)	-0601 (7)	-0303 (4)	1552 (7)	637 (17)
O (3)	3738 (6)	-0891 (3)	6208 (6)	483 (13)
O (4)	3691 (7)	-2303 (4)	4417 (7)	706 (18)
O (5)	1841 (6)	-1259 (4)	0968 (6)	551 (14)
O (6)	4495 (6)	-1812 (4)	2769 (6)	511 (14)
O (7)	3551 (6)	-0422 (4)	0842 (6)	522 (14)
C (1)	0423 (8)	0955 (4)	3927 (7)	401 (15)
C (2)	0303 (8)	0107 (5)	2017 (7)	426 (16)
C (3)	2773 (7)	-0371 (4)	2792 (6)	335 (13)
C (4)	3344 (7)	-0873 (4)	3819 (7)	337 (13)
C (5)	3451 (7)	-0555 (4)	5150 (7)	359 (14)
C (6)	2642 (9)	0749 (5)	6537 (9)	505 (19)
C (7)	3829 (7)	-1731 (5)	3713 (7)	397 (15)
C (8)	2649 (8)	-0748 (4)	1436 (8)	400 (15)
C (9)	4969 (11)	-2641 (6)	2539 (10)	690 (26)
C (10)	3554 (12)	-0826 (6)	-0421 (12)	704 (28)
C (11)	3114 (8)	2037 (5)	2864 (8)	484 (18)
C (12)	3325 (8)	1469 (5)	1890 (8)	501 (19)
C (13)	2066 (9)	1386 (6)	0944 (9)	528 (19)
C (14)	1128 (9)	1876 (5)	1376 (9)	538 (20)
C (15)	1771 (8)	2276 (5)	2568 (8)	508 (19)

* These atoms were assigned anisotropic temperature factors of the form $\exp(-2\pi^2 \times 10^{-4} \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} h_i h_j a_i^* a_j^*)$. The final values of the U_{ij} parameters are:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	314 (1)	258 (1)	281 (1)	-5 (1)	53 (1)	-1 (1)
S	371 (8)	328 (7)	299 (7)	-21 (6)	75 (6)	-15 (6)

parameters of the atoms (Table 1) were obtained by full-matrix least squares minimisation of the function $(\sum(|F_o| - |F_c|)^2/\sigma^2(F_o))$. The refinement converged $[(\Delta/\sigma) \leq 0.06]$ with R 0.036 and R_w 0.050.* Apart from regions of $\pm 2 \text{ e}\text{\AA}^{-3}$ close to the tungsten atom, probably arising from uncorrected absorption errors, the final difference synthesis was featureless. An analysis of $\langle w\Delta^2 \rangle$ with $|F_o|$ and $\sin\theta$ established the adequacy of the weighting scheme. The atomic scattering factors and the anomalous dispersion corrections for W and S atoms were taken from International Tables [6].

The calculations were carried out on the N.U.M.A.C. IBM 370 computer using the programs CAD4 (M.B. Hursthouse), X-RAY72 (J.M. Stewart), ORTEP (C.K. Johnson) and GEOM (P.R. Mallinson).

Results and discussion

Crystals of (3) are built of discrete molecules (Figure) separated from one another by van der Waals contacts.

The tungsten atom has a square-pyramidal co-ordination. The unique apical site is occupied by the centroid of the cyclopentadienyl ring. The basal co-ordination plane contains two cis carbonyl groups and a novel carbothiolic methyl ester ligand, derived by linking dimethylacetylene dicarboxylate to carbonyl and methylthio groups of the parent complex. This ligand is attached to the tungsten atom through its sulphur and terminal alkenyl carbon atoms, completing a five-membered chelate ring. The metal thus retains an 18 electron configuration in (3) and its co-ordination geometry is of a type well established both for tungsten [7 - 10] and for molybdenum [11].

* A table of the observed and calculated structure factors can be obtained from the authors on request.

The displacement of the metal atom from the cyclopentadienyl ring plane [$1.992(1) \text{ \AA}$] and the mean W-C(ring) distance [2.33 \AA] may be compared with respective values of 2.00 - 2.01 and 2.34 - 2.36 \AA found in closely related organotungsten complexes [7 - 9]. The W-C(ring) distances (Table 2) are slightly irregular, the metal atom being closest to C(13) and C(14) [$2.295(9)$ and $2.287(9) \text{ \AA}$] and furthest from C(11) [$2.384(8) \text{ \AA}$]. Despite this the cyclopentadienyl ring is, to within experimental error, a regular pentagon of side $1.416(8) \text{ \AA}$.

Table 2

Selected distances (\AA) and angles ($^\circ$)

(a) Bond lengths				
W	- S	2.440(2)	O(4) - C(7)	1.204(10)
W	- C(1)	1.969(8)	O(5) - C(8)	1.188(10)
W	- C(2)	1.950(8)	O(6) - C(7)	1.333(9)
W	- C(3)	2.194(7)	O(6) - C(9)	1.455(12)
W	- C(11)	2.384(8)	O(7) - C(8)	1.341(10)
W	- C(12)	2.340(8)	O(7) - C(10)	1.469(13)
W	- C(13)	2.295(9)	C(3) - C(4)	1.358(9)
W	- C(14)	2.287(9)	C(3) - C(8)	1.516(10)
W	- C(15)	2.342(9)	C(4) - C(5)	1.459(10)
S	- C(5)	1.814(7)	C(4) - C(7)	1.476(10)
S	- C(6)	1.799(9)	C(11) - C(12)	1.419(12)
O(1)	- C(1)	1.148(10)	C(11) - C(15)	1.400(12)
O(2)	- C(2)	1.151(10)	C(12) - C(13)	1.442(12)
O(3)	- C(5)	1.202(9)	C(13) - C(14)	1.400(13)
C(14)	- C(15)	1.418(12)		

Table 2 (continued)

(b) Bond angles

S-W-C(1)	81.8(2)	S-C(5)-C(4)	108.5(5)
S-W-C(2)	124.5(2)	S-C(5)-O(3)	119.6(6)
S-W-C(3)	72.5(2)	C(4)-C(5)-O(3)	131.7(7)
C(1)-W-C(2)	75.2(3)	C(4)-C(7)-O(4)	124.9(7)
C(1)-W-C(3)	121.0(3)	C(4)-C(7)-O(6)	112.9(6)
C(2)-W-C(3)	77.6(3)	O(4)-C(7)-O(6)	122.2(7)
W-S-C(5)	105.4(2)	C(3)-C(8)-O(5)	123.8(7)
W-S-C(6)	121.4(3)	C(3)-C(8)-O(7)	111.1(6)
C(5)-S-C(6)	100.6(4)	O(5)-C(8)-O(7)	125.1(7)
W-C(1)-O(1)	177.3(7)	C(15)-C(11)-C(12)	109.1(7)
W-C(2)-O(2)	176.4(7)	C(11)-C(12)-C(13)	106.5(7)
W-C(3)-C(4)	127.3(5)	C(12)-C(13)-C(14)	107.9(8)
W-C(3)-C(8)	116.8(5)	C(13)-C(14)-C(15)	108.6(8)
C(4)-C(3)-C(8)	115.2(6)	C(14)-C(15)-C(11)	107.8(8)
C(3)-C(4)-C(5)	117.8(6)	C(7)-O(6)-C(9)	117.5(7)
C(3)-C(4)-C(7)	125.8(6)	C(8)-O(7)-C(10)	113.0(7)
C(5)-C(4)-C(7)	116.4(6)		

(c) Torsion angles

C(3)-W-S-C(5)	-23.1(3)	C(3)-C(4)-C(5)-S	-16.5(8)
C(3)-W-S-C(6)	-136.1(4)	C(3)-C(4)-C(5)-O(3)	168.8(8)
S-W-C(3)-C(4)	20.7(6)	C(7)-C(4)-C(5)-S	165.6(5)
S-W-C(3)-C(8)	-169.0(5)	C(7)-C(4)-C(5)-O(3)	-9.2(12)
W-C(3)-C(4)-C(5)	-7.6(9)	C(4)-C(5)-S-W	28.5(5)
W-C(3)-C(4)-C(7)	170.2(5)	C(4)-C(5)-S-C(6)	155.5(5)
C(8)-C(3)-C(4)-C(5)	-178.0(6)	O(3)-C(5)-S-W	-156.0(5)
C(8)-C(3)-C(4)-C(7)	-0.3(10)	O(3)-C(5)-S-C(6)	-29.0(7)

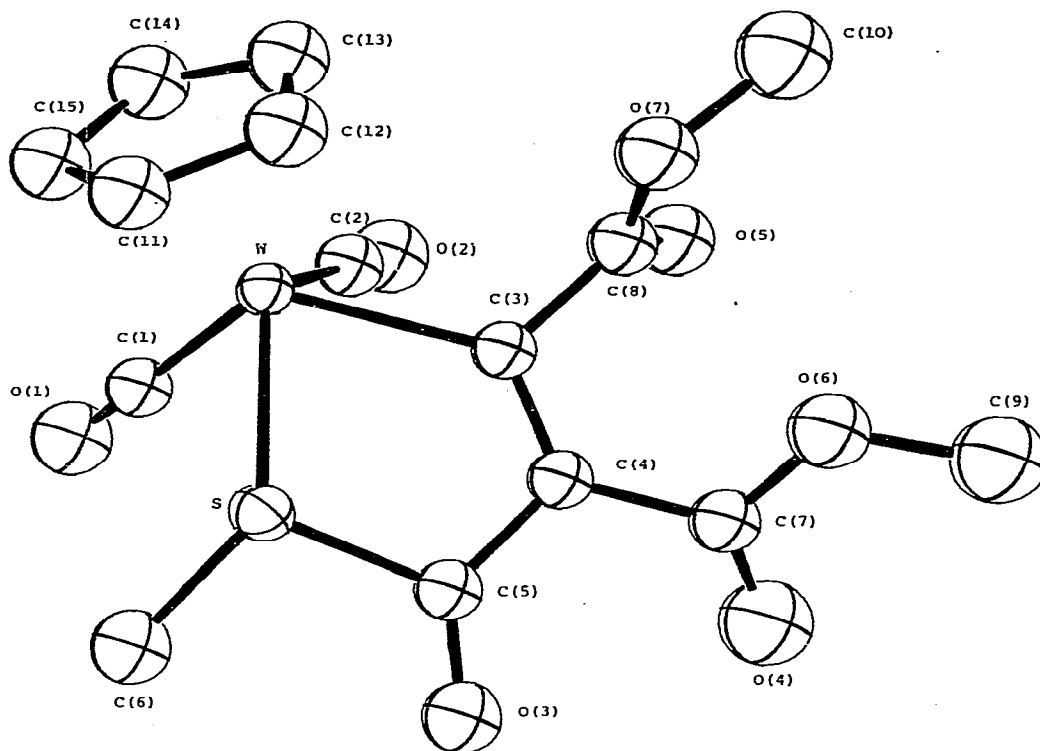


Figure A view of the molecular structure of (3) with thermal ellipsoids displaying 50% probability. Hydrogen atoms are omitted.

The formation of the chelate ring does not appear to impose any serious distortion of the basal tungsten valency angles. Thus the angles subtended at the tungsten atom by cis and trans donor atoms in the basal co-ordination plane are in the respective ranges 72.5(3) - 81.8(2) and 121.0(3) - 124.5(2)°. Corresponding angles in $[(\eta^5\text{-C}_5\text{H}_5)\text{WR}(\text{CO})_3]$ complexes are 62 - 79 and 106 - 124° when R = AuPPh₃ [7], 69 - 77 and 104 - 128° when R = Ph [8], and 62 - 83 and 102 - 124° when R = GaMe₂ [9].

The W-S bond length of 2.440(2) Å falls in the range expected for W-S single bonds. It agrees well with corresponding values

of 2.413(6) Å in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{WS}_4]$ [12] and 2.421(2) Å in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_4)]$ [13]. The W-C(alkenyl) distance of 2.194(7) Å is shorter than the W-C(ketene) distance of 2.27(2) Å in $[(\eta^5\text{-C}_5\text{H}_5)\text{W}\{\text{C}(\text{4-Me-C}_6\text{H}_4)=\text{C}=\text{O}\}(\text{CO})(\text{PMe}_3)_2]$ [10] and the W-C(phenyl) distance of 2.32(2) Å in $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{C}_6\text{H}_5)(\text{CO})_3]$ [8]. It is also short in comparison with σ -W-C distances of 2.25(3) and 2.26 Å in $[(\eta^5\text{-C}_5\text{H}_5)\text{WO}(\text{C}_6\text{H}_5)(\text{PhC}\equiv\text{CPh})]$ [14] and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{-PMe}_2\text{Ph})]\text{PF}_6$ [15]. Shortening of transition metal - carbon bonds when the donor carbon atom carries electron-withdrawing substituents has often been observed [16], and is therefore expected in (3) because of the presence of a methyl carboxylate substituent on C(3). Despite their different chemical environments the W-C(carbonyl) bond lengths are equal and agree well with corresponding distances in related structures [7 - 10]. The deviations of the W-C-O groups from linearity are slight ($<4^\circ$).

The most interesting feature of the molecular structure is the chelating ligand which incorporates the carbothiolic methyl ester function. The sulphur atom has a distorted pyramidal co-ordination. Despite the differences in hybridisation between C(5) and C(6) the S-C(5) and S-C(6) bond lengths are equal, and they fall in the range expected for S-C single bonds [17]. The remaining bond lengths and angles within the chelate ligand display no especially noteworthy feature. They are consistent with the presence of localised double bonds between C(3) and C(4) and between C(5) and O(3). The constraint imposed by the formation of the chelate ring leads to a W-C(3)-C(4)-C(5) torsion angle of $-7.6(9)^\circ$. The ring itself adopts an unsymmetrically puckered conformation, as is evident from the other internal torsion angles: $20.7(6)$, $-16.5(8)$, $28.5(5)$, and $-23.1(3)^\circ$ respectively about the bonds W-C(3), C(4)-C(5), C(5)-S, and S-W. Each methyl carboxylate group is coplanar to within ± 0.08 Å. The C(4)-C(3)-C(8)-O(5) and C(3)-C(4)-C(7)-O(4) torsion angles,

respectively 75.6(10) and $-139.5(8)^\circ$, suggest that there is little interaction between the alkene and ester π -orbitals.

In conclusion we note that the isomerisation of (1) to (3) involves an unprecedented 1,3-shift, promoted by a transition metal, of a methylthio group across an enone system.

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References

- 1 J.L. Davidson, M. Shiralian, Lj. Manojlović-Muir, and K.W. Muir, J. C. S. Chem. Comm., in the press.
- 2 F. Petillon and D.W.A. Sharp, private communication.
- 3 Lj. Manojlović-Muir, K.W. Muir, and A.N. Keith, unpublished results.
- 4 J.L. Davidson, M. Shiralian, Lj. Manojlović-Muir, and K.W. Muir, in preparation.
- 5 K.W. Muir, J. Chem. Soc. (A), (1971) 2663; Lj. Manojlović-Muir, J. Chem. Soc. (A), (1971) 2796.
- 6 'International Tables for X-Ray Crystallography', Vol IV, Kynoch Press, Birmingham, Great Britain, 1974.
- 7 J.B. Wilford and H.M. Powell, J. Chem. Soc. (A), (1969) 8.
- 8 V.A. Semion and Yu. T. Struchkov, Zh. Strukt. Khim., 9 (1968) 1046.
- 9 J.N. St. Denis, W. Butler, M.D. Glick, and J.P. Oliver, J. Organometallic Chem., 129 (1977) 1.
- 10 F.R. Kreissl, A. Frank, U. Schubert, T.L. Lindner, and G. Huttner, Angewandte Chemie International Edn., 15 (1976) 632.

- 11 Lj. Manojlović-Muir in 'Molecular Structures by Diffraction Methods', Chem. Soc. Specialist Periodical Reports, Vols 1 - 4, The Chemical Society, London, (1972 - 1975).
- 12 B.R. Davis, I. Bernal, and H. Köpf, *Angewandte Chemie International Edn.*, 10 (1971) 921.
- 13 T. Debaerdemaeker and A. Kutoglu, *Acta Cryst. (B)*, 29 (1973) 2664.
- 14 N.G. Bokiy, Yu. V. Gatilov, Yu. T. Struchkov, and N.A. Ustynyuk, *J. Organometallic Chem.*, 54 (1973) 213.
- 15 R.A. Forder, G.D. Gale, and K. Prout, *Acta Cryst. (B)*, 31 (1975) 307.
- 16 M.R. Churchill, *Perspectives in Structural Chem.*, 3 (1970) 91.
- 17 'Molecular Structures and Dimensions', Vol. A1, ed. O. Kennard, D.G. Watson, F.H. Allen, N.W. Isaacs, W.D.S. Motherwell, R.C. Pettersen, and W.G. Town, N.V.A. Oosthoek, Utrecht, (1972) 70 - 75.