is indicated. The ^1H NMR spectrum of 3 shows the phenyl protons as a complex multiplet in the range δ 7.84–7.34 (9 H) and the methoxy protons at δ 4.25 (3 H).

The ^{13}C NMR spectrum of $Os_3(*CO)_8(\mu_3,\eta^5\text{-}*C(OMe)\text{-}*C(1,2\text{-}C_6H_4*CPh))$ (each enriched site ca. 50% ^{13}C) is shown in Figure 6. There are eight carbonyl resonances in the range δ 184.6–172.1. The carbene carbon (a) is assigned to the signal at δ 242.5,[19] which shows coupling to the axial carbonyl carbon (d) at δ 184.6 (^2J(C–C) = 30 Hz), and to the adjacent carbon (b) at δ 100.8 (^2J(C–C) = 31 Hz). The carbon (b) is also coupled to a carbonyl carbon (e) at δ 176.8 (^2J(C–C) = 20 Hz). The signal at δ 191.5 is assigned to the carbon (c).

Characterization of Compound 4. The IR (Figure 5b) and ^1H NMR spectra of $Os_3(CO)_8(\mu_3,\eta^5\text{-}C(O)(OMe)C(1,2\text{-}C_6H_4CPh))$ (4) are in close agreement with those observed for $Os_3(CO)_8(\mu_3,\eta^5\text{-}C(OMe)C(1,2\text{-}C_6H_4CPh))$ (3), suggesting a related configuration for both compounds. Therefore, based on the structure determined for 3, a structure for 4 can be proposed as shown in Figure 5b, in which a C(O)OMe group replaces a COMe group. This μ-acetyl bonding mode is quite common in cluster complexes.[19,20]

Conclusions

It appears that sequential Ph^-/Me^+ treatment is effective for transformation of carbonyl ligands to alkylidene and alkylidyne moieties. Furthermore, by repeating this two-step procedure, dialkylidyne and mixed alkylidene–alkylidyne complexes can be prepared. The overall predictability of the treatment, however, is low.

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Registry No. 1, 105103-50-2; 2, 105103-51-3; 3, 105103-52-4; 4, 105121-17-3; $(\mu\text{-H})Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$, 105181-34-8; $(\mu\text{-H})Os_3(CO)_{10}(\mu_3\text{-}CPh)$, 95122-80-8; Os, 7440-04-2.

Supplementary Material Available: Tables of internuclear bond angles and anisotropic thermal parameters for compound 3 (4 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Crystal Structures of Organotungsten Complexes Formed by Sequential Insertion of Elemental Sulfur into Tungsten–Carbon Bonds

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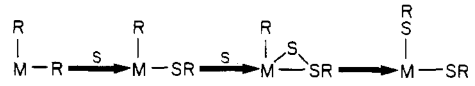
The novel organotungsten complexes $(\eta^5\text{-}C_5H_5)W(NO)(SR)R$ (1) and $(\eta^5\text{-}C_5H_5)W(NO)(\eta^2\text{-}S_2R)R$ (2) (R = CH_2SiMe_3) result from the sequential insertion of elemental sulfur into W–C σ bonds of $(\eta^5\text{-}C_5H_5)W(NO)R_2$. The molecular structures of 1 and 2 have been established by crystal structure analyses. Crystals of 1 are monoclinic, $P2_1/c$, with $a = 12.992$ (3) Å, $b = 12.726$ (1) Å, $c = 11.937$ (2) Å, $\beta = 98.810$ (8)°, and $Z = 4$; the structure was solved by conventionial heavy-atom methods and was refined by full-matrix least-squares procedures to $R = 0.036$ and $R_w = 0.044$ for 3195 absorption-corrected reflections with $I \geq 3\sigma(I)$. Crystals of 2 are also monoclinic, $P2_1/c$, with $a = 13.223$ (1) Å, $b = 12.685$ (1) Å, $c = 12.113$ (1) Å, $\beta = 92.942$ (5)°, and $Z = 4$; $R = 0.038$ and $R_w = 0.040$ for 2546 reflections. Both complexes are monomeric and possess "piano stool" molecular structures; in 1, a short (2.301 (2) Å) W–S bond indicates significant multiple-bond character in this formally 16-electron complex, while 2 is an 18-electron complex, with the $\eta^2\text{-}S_2R$ ligand functioning as a formal three-electron donor, W–S = 2.479 (2) and 2.453 (3) Å.

Introduction

Metal complexes containing chalcogenides in their framework are of synthetic and theoretical interest due to their apparent involvement in various biological and catalytic processes.[1] The experimental conditions for effecting the transformations (where M = $(\eta^5\text{-}C_5H_5)W(NO)$ and R = CH_2SiMe_3) and the characterization of the novel complexes 1–3 by conventional spectroscopic methods have been described.[2] The spectroscopic data, however, not



1 2 3

only were consistent with the formulations of 1 and 2 shown in eq 1, but also were in accord with 1 being a dimer

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Table I. Crystallographic Data

	1	2
formula[a]	$C_{13}H_{27}NOSSi_2W$	$C_{13}H_{27}NOS_2Si_2W$
fw	485.46	517.52
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	12.992 (3)	13.223 (1)
b, Å	12.726 (1)	12.685 (1)
c, Å	11.937 (2)	12.113 (1)
β, deg	98.810 (8)	92.942 (5)
V, Å^3	1950.3 (5)	2029.1 (4)
Z	4	4
D_{calcd}, g/cm^3	1.653	1.694
$F(000)$	952	1016
cryst dimens, mm	0.01 × 0.6 × 0.45	0.25 × 0.15 × 0.3
scan type	$\omega-2\theta$	$\omega-2\theta$
scan speeds, deg/min	1.1–6.7	1.3–10.1
scan range, deg in ω	0.80 + 0.35 tan θ	0.90 + 0.35 tan θ
data collected	$+h,+k,\pm l$	$\pm h,+k,+l$
$2\theta_{max}$, deg	27.5	27.5
μ(Mo Kα), cm^{-1}	63	61
transmissn factors[b]	0.075–0.54	0.27–0.48
unique reflctns	4465	4633
reflections with $I \geqslant 3\sigma(I)$	3195	2546
no. of variables	172	181
R	0.036	0.038
R_w	0.044	0.040
goodness of fit	1.47	1.44
max Δ/σ	0.004	0.12
residual density, e/A^3	−1.2 to +3.2	−0.8 to +3.0

[a] Names: **1**, (η^5-cyclopentadienyl)nitrosyl[(trimethylsilyl)methyl][(trimethylsilyl)methanethiolato]tungsten(II); **2**, (η^5-cyclopentadienyl)nitrosyl[(trimethylsilyl)methyl]{η^2-[(trimethylsilyl)methyl]disulfido}tungsten(II). [b] Most transmission factors for **1** were in the range 0.2–0.5, but a few reflections exhibited higher absorption as a result of the extreme anisotropic shape of the crystal.

with bridging SR groups[3] and with **2** possessing a M–S–S–R chain linkage. Consequently, the crystal structures of **1** and **2** have now been determined to confirm their monomeric natures and to establish unambiguously the modes of attachment of the organosulfur ligands in the solid state. The molecular structure of **3** is probably similar to that of the related 16-electron monomer (η^5-C_5H_5)Mo(NO)(SPh)$_2$.[4]

Experimental Section

X-ray Crystallographic Analyses of 1 and 2. Red-violet crystals of **1** and orange-red crystals of **2** were prepared as previously described.[2] The crystallographic data summarized in Table I were measured on an Enraf-Nonius CAD4-F diffractometer at 295 K. Lattice parameters were determined by least squares on sin θ values of 25 reflections with θ = 20–23° for **1** and 15–18° for **2**, measured with Mo Kα_1 radiation (graphite monochromator, λ = 0.70930 Å).

Table II. Positional (Fractional) and Equivalent Isotropic Thermal Parameters (U, A^2 × 10^3) for 1 and 2 with Estimated Standard Deviations in Parentheses

	x	y	z	U_{eq}
	1 (×10^4; W, S, and Si, ×10^5)			
W	8047 (2)	22737 (2)	28239 (2)	38
S	−7385 (14)	28204 (14)	17783 (17)	51
Si(1)	34204 (16)	30359 (20)	26158 (17)	56
Si(2)	−25504 (16)	21644 (17)	−293 (16)	53
N	901 (4)	3365 (5)	3761 (4)	46
O	959 (4)	4014 (4)	4511 (4)	63
C(1)	2030 (5)	2782 (5)	1952 (5)	49
C(2)	771 (6)	426 (6)	2330 (6)	56
C(3)	1783 (6)	669 (6)	2902 (6)	58
C(4)	1692 (7)	1005 (6)	4006 (6)	60
C(5)	623 (7)	988 (6)	4129 (6)	62
C(6)	82 (6)	593 (6)	3094 (7)	62
C(7)	4072 (7)	3856 (9)	1636 (9)	90
C(8)	4204 (7)	1825 (10)	2874 (9)	90
C(9)	3475 (8)	3759 (10)	3990 (9)	114
C(10)	−1237 (5)	1810 (7)	716 (6)	56
C(11)	−3459 (9)	2218 (10)	987 (9)	115
C(12)	−2956 (7)	1125 (7)	−1099 (6)	68
C(13)	−2499 (10)	3451 (8)	−726 (11)	122
	2 (×10^4; W, ×10^5)			
W	35241 (3)	45166 (3)	30817 (3)	41
S(1)	2072 (2)	3517 (2)	2235 (2)	53
S(2)	1958 (2)	5106 (2)	2097 (2)	58
Si(1)	2619 (2)	6951 (2)	4148 (2)	51
Si(2)	1299 (2)	1658 (2)	3543 (3)	62
O	3234 (5)	3816 (6)	5394 (6)	75
N	3283 (6)	4153 (5)	4462 (6)	49
C(1)	3669 (6)	6206 (6)	3516 (7)	44
C(2)	5249 (8)	4239 (11)	3233 (12)	81
C(3)	4799 (8)	3300 (9)	2914 (13)	84
C(4)	4401 (8)	3455 (12)	1836 (11)	81
C(5)	4588 (11)	4474 (14)	1538 (12)	93
C(6)	5110 (11)	4951 (11)	2405 (18)	102
C(7)	3199 (8)	8045 (8)	5009 (9)	76
C(8)	1802 (7)	6149 (8)	5033 (8)	65
C(9)	1823 (9)	7644 (9)	3050 (9)	80
C(10)	1219 (7)	3130 (8)	3281 (8)	56
C(11)	2629 (8)	1320 (9)	4036 (12)	90
C(12)	392 (8)	1404 (10)	4607 (11)	85
C(13)	950 (9)	939 (10)	2257 (11)	93

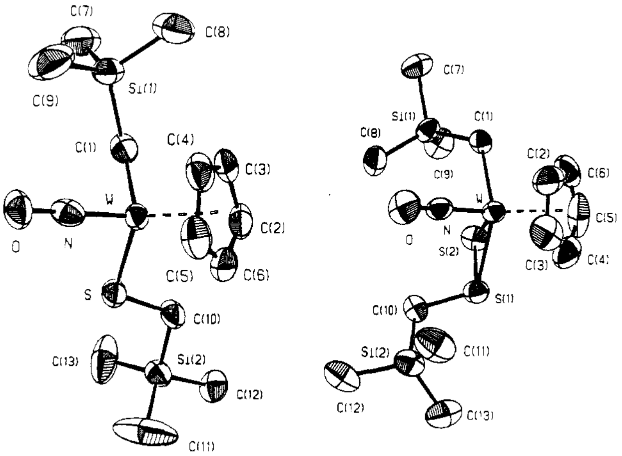

Figure 1. Views of the molecules of **1** (left) and **2** (right).

In the intensity measurements, the counter aperture was (2.0 + tan θ) × 4 mm, the scan ranges were extended 25% on both sides for background measurement, and three check reflections were monitored throughout the data collections. Data were processed,[5] including absorption corrections[6,7] and reflections with $I \geq 3\sigma(I)$ were used in the structure analyses, where $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$, where S = scan count and B = normalized background count. The structures were determined by Patterson and electron density methods and refined by full-matrix least-squares methods on F, $w = 1/\sigma^2(F)$, with scattering factors of ref 8, including anomalous dispersion corrections and anisotropic

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(5) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEPII, illustrations, by C. K. Johnson.

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(8) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, pp 99–102, 149.

Table III. Selected Bond Lengths (Å) and Angles (deg) in 1 and 2

	1	2
	Bond Lengths	
W–N	1.776 (5)	1.779 (8)
W–S/S(1)	2.301 (2)	2.479 (2)
W–S(2)		2.453 (3)
W–C(1)	2.131 (7)	2.212 (8)
W–C(Cp,av)	2.37 (1)	2.35 (1)
S(1)–S(2)		2.027 (4)
N–O	1.212 (7)	1.213 (9)
S/S(1)–C(10)	1.851 (7)	1.808 (9)
Si–C(av)	1.86 (1)	1.87 (1)
C–C(Cp,av)	1.41 (1)	1.38 (2)
	Bond Angles	
S(1)–W–S(2)		48.5 (1)
W–S(1)–S(2)		65.1 (1)
W–S(2)–S(1)		66.4 (1)
N–W–S/S(1)	94.4 (2)	94.8 (2)
N–W–C(1)	94.8 (2)	92.6 (3)
S/S(1)–W–C(1)	107.3 (2)	130.5 (2)
W–N–O	171.4 (5)	171.0 (7)
W–S/S(1)–C(10)	110.2 (2)	110.3 (3)
S(2)–S(1)–C(10)		106.3 (3)
W–C(1)–Si(1)	125.9 (3)	121.9 (4)
S/S(1)–C(10)–Si(2)	110.0 (4)	110.7 (5)
angles at Si	106.3–113.3 (5)	104.3–115.0 (5)
angles in Cp ring	106–110 (1)	106–109 (1)

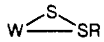
thermal parameters; H atoms were placed in calculated positions and were not refined.

Atomic positional parameters are given in Table II, selected bond lengths and angles in Table III, and other relevant data are included in the supplementary material.

Results and Discussion

The crystal structure analyses of 1 and 2 have verified their monomeric natures and revealed their "piano stool" molecular structures (Figure 1). The geometries of the (η^5-C_5H_5)W(NO)R fragments within both molecules (Table III) closely resemble that found in the parent (η^5-C_5H_5)W(NO)R_2.[9] Thus, both 1 and 2 possess essentially linear WNO groups [171.4 (5) and 171.0 (7)°] in which the short W–N [1.776 (5) and 1.779 (8) Å], and long N–O [1.212 (7) and 1.213 (9) Å] bond lengths are consistent with the existence of considerable W→NO back-bonding.[10] These structural features are also in accord with the very low ν_{NO}'s evident in the IR spectra of 1 and 2 in hexanes, i.e., 1619 and 1599 cm^{-1}, respectively.[2]

The most chemically interesting aspects of both structures involve the modes of linkage of the organosulfur ligands to the central tungsten atoms. Typical Mo–S and W–S (thiolate) distances are in the range 2.3–2.5 Å, with the shorter distances associated with metal atoms in higher oxidation states.[4,11] In 1 (formally W(II)), the thiolato group is attached by a relatively short (2.301 (2) Å) W–S bond. Consequently, although 1 may be viewed as a formal 16-electron complex,[4,9] the W–S linkage probably possesses considerable multiple-bond character as a result of S pπ→W dπ bonding; the rotational orientation of the SR group in 1 is consistent with this interpretation, the N–W–S–C(10) torsion angle being −174.6° (the corresponding N–W–S(1)–C(10) angle in 2 is 14.0°). Similar pπ–dπ bonding interactions between the thiolate lone pairs and empty metal d orbitals have been invoked to account for the unexpected stability of (η^5-C_5H_5)Mo(NO)$(SPh)_2$, also a formal 16-electron complex.[4] In contrast, the geometry of the W(η^2-S_2R) group in the alkylperthio complex 2 is quite consistent with this linkage being represented as



Thus, the W–S bonds (2.479 (2) and 2.453 (3) Å) are longer than in 1 and more in accord with the existence of W–S single bonds.[12] Furthermore, the S–S bond length of 2.027 (4) Å resembles that found for the bonds in orthorhombic sulfur (α-S), i.e., S–S(average) = 2.05 Å.[13] A few other η^2-S_2R linkages with similar geometrical features have been described previously.[14] Hence, 2 can be formulated as an 18-electron complex, with the η^2-S_2R ligand functioning as a formal three-electron donor.

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Registry No. 1, 97920-55-3; 2, 105181-26-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated hydrogen parameters, bond lengths, bond angles, and torsion angles for 1 and 2 (10 pages); listings of observed and calculated structure factors for 1 and 2 (40 pages). Ordering information is given on any current masthead page.

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