Synthesis, Structure, and Dynamic Properties of $W(S)(PhC_2Ph)(S_2CNEt_2)_2$, a Sulfidotungsten(IV) Alkyne Complex

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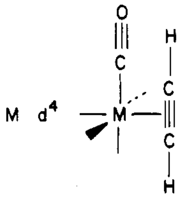
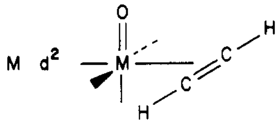
Synthesis of $W(S)(PhC_2Ph)(S_2CNEt_2)_2$ (1) has been accomplished by oxidation of $W(CO)(PhC_2Ph)(S_2CNEt_2)_2$ with cyclohexene sulfide. The molecular structure of 1 has been determined by a single-crystal X-ray diffraction study. The crystals were found to be monoclinic of space group $P2_1/n$ with $a = 10.175$ (7) Å, $b = 14.165$ (6) Å, $c = 19.279$ (39) Å, and $\beta = 94.97$ (2)°. The unit cell contains one independent molecule per asymmetric unit; the structure was refined to $R = 0.064$ and $R_w = 0.079$ with the use of 3623 reflections with $I > 3\sigma(I)$. The molecular geometry can be described as a distorted octahedron. The alkyne ligand is cis to the terminal sulfide with the C_2 unit nearly perpendicular to the W=S moiety. A rearrangement of the chelating ligands, perhaps via dissociation of the dithiocarbamate sulfur trans to the terminal sulfide to form a fluxional five-coordinate intermediate, is compatible with dynamic NMR data obtained for 1. A related minor product, $W(S)(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$, is believed to result from internal oxidative addition of one of the dithiocarbamate C–S bonds to the W(II) center of the $W(CO)(PhC_2Ph)(S_2CNEt_2)_2$ reagent.

Introduction

Properties of alkyne ligands cis to π-acceptor ligands in Mo(II) and W(II) monomers differ markedly from those of alkynes cis to π-donor ligands in related complexes. Monocarbonyl alkyne d^4 derivatives bind the alkyne tightly in a cis, parallel arrangement relative to the π-acid carbonyl ligand (see below) such that both ligands compete for back-donation from the filled $d\pi$ orbital which they share.[1] The alkyne is positioned to donate in a π fashion to the lone vacant $d\pi$ orbital, and spectroscopic properties are compatible with the four-electron donor alkyne concept,[2] as couched in molecular orbital terms,[3] for $M(CO)(RC_2R)(dtc)_2$ (M = Mo,[4] W;[5] dtc = $-S_2CNR'_2$), $Mo(CO)(RC_2R)L_2Br_2$,[6] $W(CO)(HC_2OAlCl_3)(PMe_3)_3Cl$,[7] $(\pi\text{-}C_5H_5)M(CO)(RC_2R)X$ (M = Mo, W; X = Cl,[8] SPh[9]) and $(\pi\text{-}C_5H_5)W(CO)(RC_2R)R'$ ($R' = CH_3$).[10]

Oxo analogues are know for some of these carbonyl compounds: $M(O)(RC_2R)(dtc)_2$ (M = Mo,[11] W[12]), $(\pi\text{-}C_5H_5)W(O)(PhC_2Ph)Ph$,[13] and $(\pi\text{-}C_5H_5)Mo(O)(CF_3C_2CF_3)(SPh)$.[14] The alkyne ligand in these is less tightly bound with a cis, perpendicular geometry relative to the M=O unit (see below) such that both ligands compete to donate in a π fashion to the vacant $d\pi$ orbital which they share. The alkyne is positioned to stabilize the lone filled $d\pi$ orbital through acceptance into the $\pi_{\parallel}{}^*$ orbital. In addition to these oxo complexes of Mo and W and $Re(O)I(RC_2R)_2$[15] an extensive series of W(IV) halo and alkyl alkyne complexes has been prepared.[16]





We wish to report the synthesis and characterization of a W(IV) sulfide alkyne complex, $W(S)(PhC_2Ph)(dtc)_2$ (1). Structural parameters and static and dynamic NMR spectroscopy combine with data available for $W(O)(RC_2R)(dtc)_2$ complexes to allow comparison of terminal oxide and terminal sulfide π-donor properties. The electronic versatility of both alkyne and dithiocarbamate ligands is evident in this work. A minor product, formulated as $W(S)(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$, has been isolated from the reaction mixture. Other examples of oxidative cleavage of dithiocarbamate C–S bonds to form a thiocarboxamido ligand have been reported.[17] A molecular orbital description of the two monomers described here is facilitated by reference to the MO picture of the $(dtc)_2Mo(\mu\text{-}S)(\mu\text{-}RC_2R)Mo(dtc)(dtca)$ (dtca = $SCNR_2$) dimer[18] which can be constructed mentally by merging the two monomers described herein into a dimer such that superposition of the redundant alkyne and sulfur ligands forms the bridging ligands.

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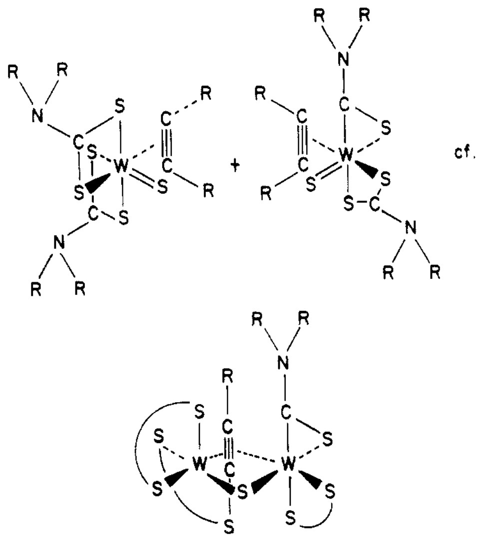

Experimental Section

Materials and Methods. All reactions were performed under an inert atmosphere using standard Schlenk techniques. Solvents were degassed prior to use. Tungsten hexacarbonyl, diphenylacetylene, dialkyldithiocarbamates, and cyclohexene sulfide were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Beckman IR 4250 and calibrated with a polystyrene standard. ^{1}H and ^{13}C NMR were recorded on a WM Brüker 250 spectrometer. NMR sample temperatures were measured by a thermocouple located near the probe. Elemental analyses were performed by Galbraith Laboratories of Knoxville, TN.

Syntheses. $W(CO)(PhC_2Ph)(detc)_2$. $W(CO)_3(detc)_2$ (detc = S_2CNEt_2) was synthesized from $[W(CO)_4I_3]^-$ as recently reported.[19] A threefold excess of diphenylacetylene was added to a CH_2Cl_2 solution of $W(CO)_3(detc)_2$ (10^{-2} M) and stirred for 3 h to yield a dark green solution of $W(CO)(PhC_2Ph)(detc)_2$. Crystallization was induced by addition of methanol and cooling to -20 °C. Air-stable forest-green crystals were isolated in greater than 70% overall yield from the initial tungsten hexacarbonyl reagent.

$W(S)(PhC_2Ph)(detc)_2$ and $W(S)(PhC_2Ph)(detc)(dtca)$. A solution of $W(CO)(PhC_2Ph)(detc)_2$ (detc = S_2CNEt_2) (0.80 g, 1.16 mmol) and cyclohexenyl sulfide (0.133 g, 1.16 mmol) in toluene was refluxed for 10 min. Reaction was complete as judged by disappearance of the reagent CO absorption in the infrared spectrum. The solution was cooled, reduced to 3 mL in vacuo and chromatographed on a large Florisil column. A bright yellow band was removed with toluene. A second, red-orange fraction was eluted with a 1:1 toluene/methylene chloride mixture. Both products were reduced to oils in vacuo. Crystallizations were induced by cooling a methylene chloride/hexane solution to -20 °C. The first column fraction yielded bright orange crystals of $W(S)(PhC_2Ph)(detc)(dtca)$ (dtca = $SCNEt_2$) in 10% yield. The second fraction produced red-orange crystals of $W(S)(PhC_2Ph)(detc)_2$ in 30% yield. Both products are relatively air stable in solution and as solids.

$W(S)(PhC_2Ph)(detc)_2$: ^{1}H NMR ($CDCl_3$) δ 0.96–1.36 (t, 12 H, CH_3), 3.26 (m, 1 H, CH_2), 3.42 (m, 2 H, CH_2), 3.63–3.95 (m, 5 H, CH_2), 7.12–7.87 (m, 10 H); ^{13}C NMR (acetone-d_6) δ 12.1, 12.5, 13.2 (CH_3), 45.0, 45.5, 46.0, 46.5 (CH_2), 128.1, 128.3, 129.5, 129.7, 131.7, 139.2, 141.6 (phenyl), 177.6, 184.4 ($C{\equiv}C$), 203.5, 204.2 (S_2CNEt_2); IR (KBr) ν_{C-N} 1502 cm^{-1}, $\nu_{W=S}$ 485 cm^{-1}.

$W(S)(PhC_2Ph)(detc)(dtca)$: ^{1}H NMR ($CDCl_3$) δ 0.69 (t, 3 H, CH_3), 1.33 (m, 6 H, CH_3), 1.48 (m, 3 H, CH_3), 3.62–3.93 (m, 6 H, CH_2), 4.09 (m, 1 H, CH_2), 4.84 (m, 1 H, CH_2), 7.17–7.84 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 12.3, 12.9, 14.2 (CH_3), 45.2, 50.3, 54.4 (CH_2), 127.3, 127.6, 128.2, 128.4, 130.6, 139.7 (phenyl), 163.0, 176.9 ($C{\equiv}C$), 207.1 (S_2CNEt_2), 257.5 ($SCNEt_2$); IR (KBr) ν_{C-N} 1560, 1545, 1533 cm^{-1}, $\nu_{W=S}$ 490 cm^{-1}. Anal. Calcd for $WS_4N_2C_{24}H_{30}$: W, 27.91; S, 19.47; N, 4.25; C, 43.77; H, 4.59. Found: W, 27.84; S, 19.62; N, 4.30; C, 43.83; H, 4.62.

Table I. Crystallographic Data for $W(S)(PhC_2Ph)(detc)_2$

Crystal Data	
mol formula	$WS_5N_2C_{24}H_{30}$
fw	690.44
space group	$P2_1/n$
cell parameters	
a, Å	10.175 (7)
b, Å	14.165 (6)
c, Å	19.279 (39)
β, deg	94.97 (2)
vol, Å^3	2768 (9)
ρ(calcd), g/cm^3	1.657
Z	4
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.710 73)
linear abs coeff, cm^{-1}	48.0
scan type	$\omega/1.67\theta$
scan width, deg.	$1.10 + 0.35 \tan \theta$
background	25% of full scan width on both sides
θ limits	$1° < \theta < 25°$
quadrants collected	$\pm h,+k,+l$
unique data	5069
data with $I \geqslant 3\sigma(I)$	3623
R	0.064
R_w	0.079
largest parameter shift	0.25
error in an observn of unit wt	5.51

Calculations. The extended Hückel method was employed in this study. Program number QCPE358 from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, was used for these calculations. Values used in these calculations were obtained from published sources.[20] The crystallographic coordinates of $W(C_2H_2)(CO)(dmtc)_2$[5a] were used to establish the dithiocarbamate geometry. The N—H distance for S_2CNH_2 was set at 1.05 Å with the C=C bond distance of bound HC_2H at 1.29 Å. Bond distances of 1.70 and 2.15 Å were used for Mo=O and Mo=S, respectively.

Collection of Diffraction Data. Crystals of $W(S)(PhC_2Ph)(detc)_2$ were grown from a dichloromethane solution under a layer of cyclohexane. An orange prism having approximate dimensions 0.75 × 0.85 × 0.20 mm was mounted on a glass wand and coated with epoxy cement. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[21] A monoclinic cell was indicated by 25 centered reflections found in the region $30° < 2\theta < 34°$ and refined by least-squares calculations. The cell parameters are listed in Table I. Although axial scans revealed twinning along the $h00$ axis, the degree of twinning was slight and did not interfere with the subsequent solution of the crystal structure.

Diffraction data were collected in the quadrant $\pm h,+k,+l$ under the conditions specified in Table I. Three standard reflections were monitored for decay every 5 h, and the crystal was recentered as necessary every 500 reflections. A total of 5069 data were processed and corrected for Lorentz-polarization effects. Psi scans with nine reflections having $80° < \chi < 90°$ were performed to provide an empirical correction for absorption. The observed transmission factors, which ranged from 75 to 100%, reflect the geometry of the crystal as well as the large absorption coefficient of tungsten. A total of 3623 reflections having $I > 3\sigma(I)$[22] were used in the solution and refinement of the structure.

Solution and Refinement of the Structure. Inspection of the data revealed systematic absences for $h0l$ ($h + l = 2n + 1$)

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[21] Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package.

[22] $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$ where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count, and ρ = 0.01 is a correction factor.

Table II. Final Atomic Positional Parameters for W(S)(PhC$_2$Ph)(S$_2$CNEt$_2$)$_2$

atom	x^a	y	z
W	−0.01409 (7)	0.28252 (5)	0.15741 (4)
S1	−0.2045 (4)	0.2819 (4)	0.1006 (3)
S2	0.0375 (4)	0.4248 (3)	0.0875 (3)
S3	0.2366 (4)	0.3341 (3)	0.1789 (3)
S4	0.0883 (5)	0.1904 (3)	0.0595 (3)
S5	0.0435 (5)	0.1243 (3)	0.1943 (3)
N1	0.283 (1)	0.492 (1)	0.1080 (8)
N2	0.135 (1)	0.010 (1)	0.0984 (7)
C1	0.201 (1)	0.423 (1)	0.123 (1)
C2	0.247 (2)	0.569 (1)	0.060 (1)
C3	0.200 (2)	0.653 (2)	0.099 (1)
C4	0.420 (2)	0.490 (1)	0.142 (1)
C5	0.512 (2)	0.435 (2)	0.098 (2)
C6	0.096 (2)	0.096 (1)	0.116 (1)
C7	0.133 (2)	−0.068 (1)	0.151 (1)
C8	0.007 (2)	−0.119 (2)	0.149 (1)
C9	0.183 (2)	−0.012 (1)	0.031 (1)
C10	0.327 (2)	−0.000 (2)	0.031 (1)
C11	−0.066 (1)	0.289 (1)	0.260 (1)
C12	−0.027 (2)	0.373 (1)	0.241 (1)
C13	−0.110 (2)	0.239 (1)	0.320 (1)
C14	−0.203 (2)	0.167 (1)	0.311 (1)
C15	−0.258 (2)	0.124 (2)	0.359 (1)
C16	−0.223 (2)	0.149 (2)	0.423 (2)
C17	−0.130 (3)	0.219 (2)	0.440 (1)
C18	−0.069 (2)	0.265 (2)	0.386 (1)
C19	−0.027 (2)	0.467 (1)	0.272 (1)
C20	−0.122 (2)	0.492 (1)	0.316 (1)
C21	−0.126 (2)	0.577 (1)	0.344 (1)
C22	−0.030 (2)	0.641 (1)	0.333 (1)
C23	0.066 (2)	0.621 (1)	0.288 (1)
C24	0.066 (2)	0.534 (1)	0.260 (1)

[a] Numbers in parentheses are the estimated standard deviations of the coordinates and refer to the last significant digit of the entry.

and 0*k*0 ($k = 2n + 1$) suggesting the space group $P2_1/n$, which was verified by successful structure determination. The single tungsten atom was located in a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were obtained from subsequent Fourier and difference Fourier calculations. Idealized hydrogen positions were calculated (d(C–H) = 0.95 Å). Refinement allowing the 32 non-hydrogen atoms to vary anisotropically and including the 30 hydrogens in fixed, idealized positions converged with the largest parameter shift 0.77, $R = 0.064$, and $R_w = 0.079$.[23]

Results

Cyclohexenyl sulfide reacts with W(CO)(PhC$_2$Ph)(detc)$_2$ (detc = $^-$S$_2$CNEt$_2$) in refluxing toluene to form W(S)(PhC$_2$Ph)(detc)$_2$ (1) which was isolated as orange crystals in 30% yield following solvent removal, Florisil chromatography, and recrystallization from methylene chloride/cyclohexane solution. A second crystalline product believed to be W(S)(PhC$_2$Ph)(detc)(dtca) (2) (dtca = $^-$SCNR$_2$) was isolated in 10% yield. In the absence of cyclohexene sulfide the W(CO)(PhC$_2$Ph)(detc)$_2$ reagent decomposes in refluxing toluene to afford only a trace of 2 and no 1; more than 1 equivalent of cyclohexenyl sulfide or S$_8$ decreases the yield of 1 dramatically.

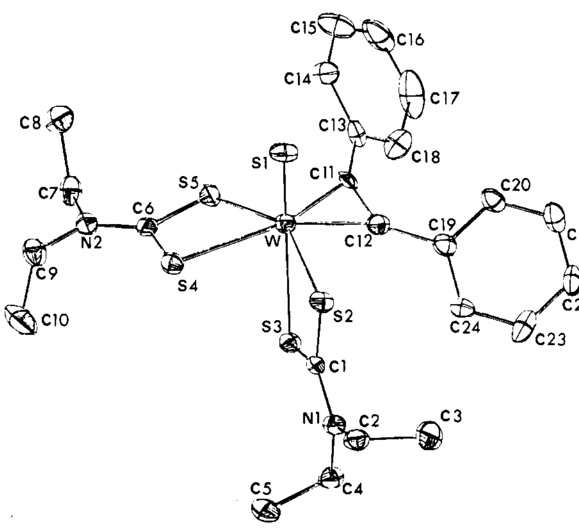

Figure 1. The molecular structure of W(S)(PhC$_2$Ph)(S$_2$CNEt$_2$)$_2$ showing the atomic labeling scheme.

Table III. Selected Bond Distances (Å) in W(S)(PhC$_2$Ph)(S$_2$CNEt$_2$)$_2$

W–S1	2.147 (2)	S4–C6	1.727 (7)
W–S2	2.507 (2)	S5–C6	1.710 (8)
W–S3	2.648 (2)	C1–N1	1.321 (8)
W–S4	2.582 (2)	C6–N2	1.308 (8)
W–S5	2.409 (2)	N1–C2	1.46 (1)
W–C11	2.093 (6)	N1–C4	1.49 (1)
W–C12	2.065 (7)	N2–C7	1.48 (1)
C11–C12	1.31 (1)	N2–C9	1.46 (1)
C11–C13	1.45 (1)	C2–C3	1.52 (1)
C12–C19	1.46 (1)	C4–C5	1.52 (1)
S2–C1	1.744 (6)	C7–C8	1.51 (1)
S3–C1	1.691 (7)	C9–C10	1.49 (1)

Table IV. Selected Bond Angles (deg) in W(S)(PhC$_2$Ph)(S$_2$CNEt$_2$)$_2$

S1–W–S2	87.2 (1)	C11–C12–C19	134.8 (7)
S1–W–S3	153.7 (1)	C12–C11–C13	141.6 (7)
S1–W–S4	91.6 (1)	W–C12–C19	151.5 (6)
S1–W–S5	109.4 (1)	W–C11–C13	147.8 (5)
S1–W–C11	101.1 (2)	W–C11–C12	70.5 (4)
S1–W–C12	106.6 (2)	W–C12–C11	72.8 (4)
S2–W–S3	67.6 (1)	S2–C1–S3	113.3 (4)
S2–W–S4	84.1 (1)	S4–C6–S5	111.0 (4)
S2–W–S5	148.3 (1)	S2–C1–N1	121.0 (5)
S2–W–C11	123.7 (2)	S3–C1–N1	125.7 (5)
S2–W–C12	87.5 (2)	S4–C6–N2	124.6 (6)
S3–W–S4	78.9 (1)	S5–C6–N2	124.4 (6)
S3–W–S5	90.3 (1)	C1–N1–C2	122.6 (6)
S3–W–C11	99.2 (2)	C1–N1–C4	119.0 (6)
S3–W–C12	80.6 (2)	C6–N2–C7	119.5 (6)
S4–W–S5	69.1 (1)	C6–N2–C9	122.7 (7)
S4–W–C11	149.6 (2)	N1–C2–C3	110.6 (7)
S4–W–C12	159.5 (2)	N1–C4–C5	110.7 (7)
S5–W–C11	80.6 (2)	N2–C7–C8	113.9 (7)
S5–W–C12	112.0 (2)	N2–C9–C10	112.1 (7)
C11–W–C12	36.6 (3)		

The solid-state structure of sulfido(diphenylacetylene)bis(diethyldithiocarbamate)tungsten(IV) is shown in Figure 1 where the atomic numbering scheme is defined. Final positional parameters for all non-hydrogen atoms are listed in Table II. The geometry can be viewed as a distorted octahedron with the alkyne occupying one coordination site. An alternative description as a pentagonal bipyramid places the sulfido ligand S1 and dithiocarbamate S3 in axial positions with the remaining three sulfur atoms and the two alkyne carbons constituting the equatorial belt. The tungsten atom is displaced 0.33 Å above the pentagonal plane toward S1, and the S1–W–S3 angle of 153.7° deviates substantially from the linear arrangement of axial ligands of the idealized geometry. The diphenylacetylene ligand adopts a normal cis bent geometry. The two phenyl rings are canted 33.8 and 35.9°, respectively, relative to the W–C11–C12 plane. Bond distances and angles are listed in Tables III and IV, respectively.

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[23] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(F_o^2)]^2$ and $\sigma(F_o^2) = [\sigma^2(I) + \rho^2 I^2]^{1/2}$ with ρ assigned a value of 0.01. The residuals are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$.

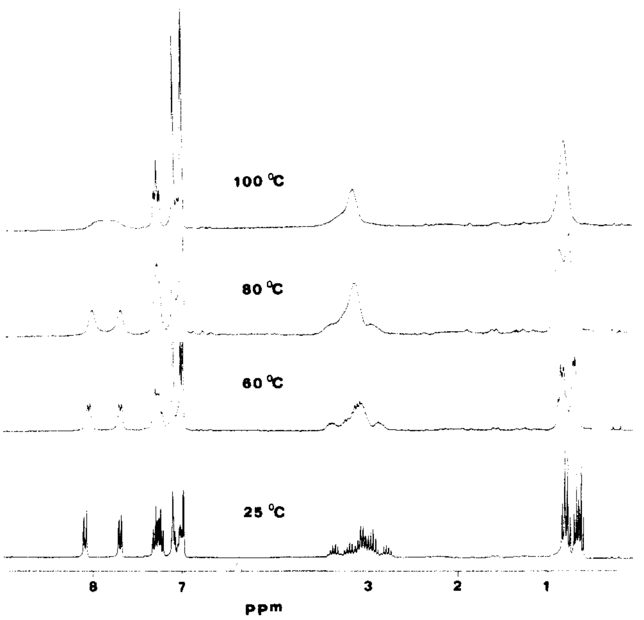


Figure 2. Representative variable-temperature ^{1}H NMR spectra of $W(S)(PhC_2Ph)(S_2CNEt_2)_2$ from 25 to 100 °C in *p*-xylene.

The most informative infrared absorptions for 1 occur at 488 cm^{-1}, assigned to the W=S dominated normal mode, and 1502 cm^{-1}, attributed to the dithiocarbamate C—N stretch. An intense absorption in 2 at 490 cm^{-1} is assigned by analogy as a W=S stretch while absorptions at 1545 and 1533 cm^{-1} reflect the presence of the thiocarboxamido C—N linkage as well as the dithiocarbamate C—N unit. Very weak absorptions at 1745 and 1765 cm^{-1} are present in 1 and 2, respectively, and may be the C≡C stretch of the coordinated diphenylacetylene.

The carbon-13 NMR spectrum of 1 exhibited normal chemical shifts for the phenyl and ethyl groups of the alkyne and dithiocarbamate ligands. Additional weak signals at 203.5 and 204.2 ppm can be assigned to the central carbons of the two distinct chelating ligands with the two remaining resonances at 177.6 and 184.4 ppm attributed to the bound alkyne carbons. The alkyne carbons of 2 are also near this chemical shift range (163.0 and 176.9 ppm), but only one central dithiocarbamate resonance is observed (207.1 ppm). A single low field signal at 257.5 ppm is assigned to the metal-bound carbon of the newly formed thiocarboxamido ligand in 2 based on literature values for thiocarboxamido ligands.[18,24]

A dynamic process is evident in ^{1}H NMR spectra of 1 recorded as a function of increasing temperature in *p*-xylene (Figure 2). At 30 °C four upfield triplets above 1 ppm correspond to the four inequivalent methyl groups of the dithiocarbamate ethyl substituents. Note that the planarity of the S_2CNC_2 fragment ensures that the alkyl groups mimic the sulfur environments, i.e., one is trans to alkyne, one is trans to sulfide, and two are trans to one another but strongly differentiated by the orientation of the chelate linkage, one to the axial and the other to an equatorial site. The four inequivalent sets of diastereotopic methylene protons overlap to form a complex pattern around 3 ppm. The phenyl protons range from 7 to 8 ppm, and two resonances (crude doublets with secondary coupling and integrating to 2 protons each) are segregated well downfield of the remaining phenyl signals. The methyl signals broaden and coalesce as the temperature is increased as do the methylene signals. The downfield phenyl protons exchange with one another, and a complex multiplet in the phenyl region is transformed to a crude triplet at high temperature. Activation energies were calculated for the methyl exchange and both phenyl averaging processes from rate constants estimated at their respective coalescence temperatures ($k_{ex} = \pi(\Delta\nu_{AB})/(2)^{1/2}$ at T_c).[25] Activation energies were also calculated for the exchanging phenyl protons from the slow-exchange line broadening approximation, $k_{ex} = \pi\Delta w_{1/2}$[25] (see Table V).

Table V. Activation Barriers Calculated for $W(S)(PhC_2Ph)(S_2CNEt_2)_2$

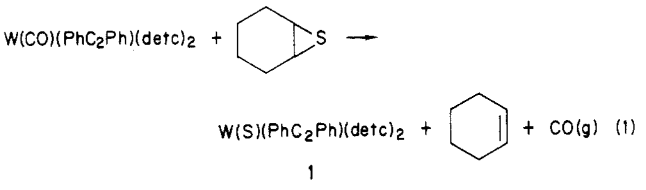
site probed	T, K	k_{ex}, s^{-1}	$\Delta G^{\ddagger}$, kcal/mol^{-1}
$S_2CN(CH_2CH_3)_2$	358	79	18.0[a]
PhC_2Ph (7.7, 8.1 ppm)	373	129	18.4[a]
	353	35	18.3[b]
	333	12	17.9[b]
PhC_2Ph (7.25 ppm)	348	68	17.6[a]
			18.0 ± 0.4

[a] Calculated at the coalescence temperature as listed. [b] Calculated from the slow-exchange approximation at the temperature listed.

Discussion

Synthesis. Alkyne ligands in monomeric molybdenum and tungsten complexes prefer to confront one filled and one vacant dπ orbital in addition to a vacant σ receptor orbital. When the alkyne is counted as a neutral ligand, only d^2 and d^4 configurations present optimal dπ electron distributions for diamagnetic octahedral complexes. An extensive chemistry of Mo(II) and W(II) d^4 alkyne derivatives has developed during the past few years.[1-10] One general route to higher oxidation state metal oxo alkyne complexes is exemplified by the oxidation of $W(CO)(RC_2R)(dtc)_2$ with a dimeric Mo(V) oxygen atom transfer reagent, $Mo_2O_3[S_2P(OEt)_2]_4$, to form $W(O)(RC_2R)(dtc)_2$.[12] Alternatively one can substitute an alkyne ligand into a high oxidation state metal reagent as illustrated by the preparation of a series of W(IV) alkyne complexes derived from $WCl_4(RC_2R)$.[16]

Cyclohexenyl sulfide, a sulfur atom transfer reagent, reacts with $W(CO)(PhC_2Ph)(detc)_2$ and oxidizes W(II) to W(IV) with loss of carbon monoxide (eq 1). Dissociation



of carbon monoxide may initiate this reaction; the analogous Mo(II) reagent $Mo(CO)(PhC_2Ph)(dtc)_2$ reversibly dissociates CO at room temperature[26] and irreversibly decomposes with complete loss of CO in 30 min at 90 °C.

Qualitative Molecular Orbital Description. The conceptual simplicity of an octahedral bonding description is appropriate for 1 when the alkyne is considered to occupy a single coordination position, and the molecular orbital scheme which results (Figure 3) is qualitatively analogous to schemes presented for $M(O)(RC_2R)(dtc)_2$[12] and other d^2 oxo alkyne monomers.[14] The two metal dπ electrons reside in the d$_{xy}$ orbital which is stabilized by back-bonding into the vacant alkyne $\pi_{\parallel}^*$ orbital while both

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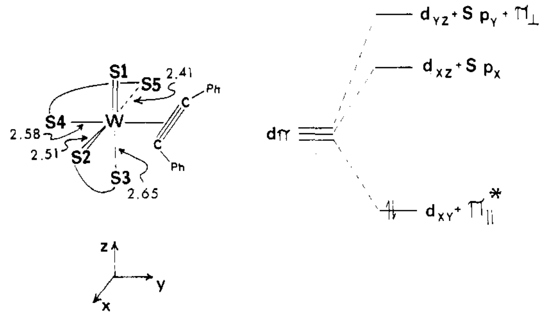

Figure 3. Schematic representation of $W(S)(PhC_2Ph)(S_2CNEt_2)_2$ and a qualitative MO diagram of the $d\pi$ dominated orbitals.

S^{2-} perpendicular p orbitals and the filled alkyne $\pi_\perp$ orbital serve as π donors into vacant $d\pi$ orbitals.

Structure. The most informative features of the structure of 1 are the metal–ligand bond distances. The W—S1 terminal sulfide bond length of 2.147 (2) Å is compatible with a simple valence bond W═S description and can be compared to other W═S distances of 2.086 Å in $WSCl_4$ in the gas phase,[27] 2.132 Å in $[WSCl_5]^-$,[28] and 2.16 Å in $[WS_4]^{2-}$.[29] The normal influences of shorter bond distances with decreasing metal coordination numbers, increasing metal oxidation states, and decreasing competition among π-donor ligands no doubt all play a role in determining the W═S distance. For comparison terminal Mo═S bond lengths in Mo(V) dimers normally lie between 2.08 and 2.13 Å.[30]

The average W—C bond length to the alkyne ligand of 2.08 Å in 1 is comparable to distances in other Mo and W monomers where there is competition for vacant metal $d\pi$ orbitals ($(\pi\text{-}C_5H_5)W(O)(PhC_2Ph)Ph$, 2.11 Å;[13] $(\pi\text{-}C_5H_5)Mo(O)(CF_3C_2CF_3)(SC_6F_5)$, 2.10 Å;[14] $Mo(O)(RC_2R)(dmtc)_2$, R = COC_6H_5Me, 2.12 Å;[11a] $Mo(MeC_2Me)_2(S_2CNC_4H_4)_2$, 2.05 Å;[31] $(\pi\text{-}C_5H_5)W(CF_3C_2CF_3)_2Cl$, 2.06 Å[32]) and longer than metal–alkyne bonds where there is no strong π-donor competition from other ligands ($W(CO)(HC_2H)(detc)_2$, 2.03 Å;[5a] $(\pi\text{-}C_5H_5)Mo(CO)(CF_3C_2CF_3)(SC_6F_5)$, 2.03 Å;[14] $W(CO)(HC_2OACl_3)(PMe_3)_3Cl$, 2.02 Å;[7] $Mo(CO)(PhC_2H)(PEt_3)_2Br_2$, 1.99 Å[6]). In particular the diphenylacetylene is bound more tightly in 1 than in the W(IV) oxo complex $(\pi\text{-}C_5H_5)W(O)(PhC_2Ph)Ph$.[13] The difference in ancillary ligands invalidates definitive comparisons, but certainly the available structural data support the hypothesis that the alkyne ligand competes more effectively as a π donor vs. sulfide than vs. oxide.

The angle between the W═S unit and the cis, perpendicular alkyne is 104°. An obtuse angle between cis π-donor ligands is common in octahedral complexes: $Mo(O)_2(dtc)_2$, 105.7°;[33] $Mo(O)(RC_2R)(dmtc)_2$, R = COC_6H_5Me, 101.3°;[11a] $(\pi\text{-}C_5H_5)Mo(O)(CF_3C_2CF_3)(SC_6F_5)$, 105°;[14] $Mo(MeC_2Me)_2(S_2CNC_4H_4)_2$, 99°.[31] In a VSEPR model this simply reflects the greater spatial requirements of multiple metal–ligand bonds, but it is interesting to note that cis π-acceptor ligands, which also build some multiple-bond character into the metal–ligand link, do not exhibit obtuse angles: cf. $Mo(O)_3(dien)$, 106°[34] and $Mo(CO)_3(dien)$, 85°.[35]

Table VI. Representative Carbon-13 Chemical Shifts for Alkyne Carbons Bound to Molybdenum and Tungsten

complex	δ_{av}	ref
$(\pi\text{-}C_5H_5)_2Mo(CH_3C_2CH_3)$	115	41
$(\pi\text{-}C_5H_5)_2Mo(HC_2H)$	118	*a*
$W(O)(HC_2H)(detc)_2$	150	12
$W(S)(PhC_2Ph)(detc)(SCNEt_2)$	170	this work
$Mo(HC_2\text{-}n\text{-}Bu)_2(dmtc)_2$	179	42
$W(S)(PhC_2Ph)(detc)_2$	180	this work
$W(CO)(EtC_2Et)_3$	181	41
$[W(PhC_2Ph)_3SnPh_3]$	190	*b*
$Mo(CO)(HC_2H)(dmtc)_2$	204	41
$W(CO)(HC_2H)(detc)_2$	207	41
$Mo(CO)(PhC_2H)(PEt_3)_2Br_2$	225	6
$W(EtC_2Et)(Me)_3Cl$	240	16
$[W(EtC_2Et)Cl_5]$	284	16

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The W–S dithiocarbamate distances range from 2.41 to 2.65 Å with the longest bonds opposite the high trans influence sulfide and alkyne ligands at 2.65 and 2.58 Å, respectively. Perhaps more surprising is the discrepancy of 0.10 Å between the two dithiocarbamate sulfur donors trans to one another. The influence of selective π donation, recognized earlier in $Mo_2(\mu\text{-}S)(\mu\text{-}RC_2R)(dtc)_3(dtca)$,[18] is reflected in these bond distances. The flexible π-donor capability of dithiocarbamate ligands results in M–S bond length variations of this magnitude depending on whether the chelate π system encounters a filled or vacant metal $d\pi$ orbital. In 1 the p_π orbital of S2, as dictated by linking the chelate axially via S3, overlaps the filled d_{xy} orbital while the p_π orbital of S5, trans to S2, overlaps the vacant d_{xz} orbital. The W–S5 bond at 2.41 Å reflects π donation from the chelate while the W–S2 distance of 2.51 Å is typical of tungsten–dithiocarbamate bonds where π donation is not accessible. A similar pattern of Mo–S dithiocarbamate distances is apparent in $Mo(O)(S_2)(dtc)_2$[36] and should apply to $Mo(O)((NC)_2C_2(CN)_2)(dtc)_2$,[37] although Mo–S distances were not individually specified in the structural report for the latter compound. For d^4 complexes such as $W(CO)(HC_2H)(dtc)_2$ in an analogous coordinate system the d_{xy} orbital is vacant and d_{xz} is filled with the alkyne parallel to the CO ligand.[5a] A reversal of W–S bond lengths is expected and observed. Maintaining the S atom numbering scheme of Figure 3 gives W–S2 = 2.40 Å and W–S5 = 2.55 Å for $W(CO)(HC_2H)(dtc)_2$.[5a]

Infrared and NMR Spectra. The relatively low frequency of 490 cm^{-1} observed for the W═S stretching mode in 1 probably reflects competitive π donation from the alkyne and dithiocarbamate ligands. Higher frequencies characterize higher oxidation state tungsten chloride derivatives ($WSCl_4(thf)$, 558 cm^{-1};[38] $WSCl_4$, 568 cm^{-1};[39] $WSCl_4(py)$, 541 cm^{-1};[38] $WSCl_3(bpy)$, 531 cm^{-1}[38]) with W═S terminal units in $W_3S_9^{2-}$ trimers displaying comparable frequencies of 492 and 479 cm^{-1}.[40]

Carbon-13 chemical shifts have been roughly correlated with the extent of π donation from the filled alkyne $\pi_\perp$ orbital to the metal[41] (see Table VI). The ^{13}C δ value of

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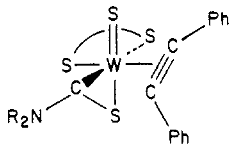
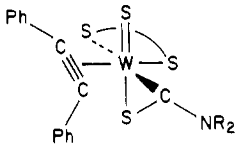
180 ppm (average) for 1 lies between four-electron and two-electron donor alkyne limits and is quite close to the 179 ppm shift of $Mo(HC_2$-n-$Bu)_2(dmtc)_2$[42] where symmetry dictates that both alkynes donate equally to the vacant dπ orbital; i.e., these are "three-electron" donor alkyne ligands. The alkyne carbons of $W(O)(HC_2H)(detc)_2$ resonate at 150 ppm (average)[12] in accord with the suggestion that the alkyne is a more effective π donor in the sulfide complex 1.

Averaging of the two alkyne phenyl signals and of all four dithiocarbamate alkyl groups occurs on the NMR time scale with a calculated activation energy near 18.0 kcal/mol. Although it may be that the onset of alkyne rotation relative to the metal fragment or rotation around the C–N bond of the chelates is coincident with the major dynamic process, neither rapid alkyne rotation nor rapid rotation around the C–N bonds (nor the combination of both processes) will cause all four alkyl groups to equilibrate. In fact alkyne rotation and C–N bond rotation are independent of one another in that rapidly spinning the alkyne will not influence the dithiocarbamate signals and pairwise alkyl exchange via C–N bond rotation will have no effect on the alkyne substituent signals.

In analogy to the fluxional process in $W(O)(RC_2R)(dtc)_2$ complexes[12] where $\Delta G^{\ddagger}$ is between 15 and 16 kcal/mol, a dechelation of one dithiocarbamate terminus followed by rearrangement of the five-coordinate intermediate offers a simple mechanism compatible with the observed dynamic behavior. The long W–S bond trans to the terminal sulfide and oxide suggests a large trans effect for these ligands, and indeed the activation energy is slightly higher for the shorter W–S bond trans to sulfide (cf. 2.65 to 2.70 Å). Extended Hückel calculations for $Mo(S)(HC_2H)(S_2CNH_2)_2$ predict an alkyne rotational barrier of 19.3 kcal/mol. Regardless of the numerical accuracy of these calculations they affirm the preferential alkyne orientation that could lead to a higher barrier for rotation than for dechelation of a dithiocarbamate.

$W(S)(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$ (2). The correspondence between 1 and 2 and the $(dtc)_2Mo(\mu$-$S)(\mu$-$RC_2R)Mo(dtc)(dtca)$ (dtca = dialkylthiocarboxamido, $SCNR_2$) dimers reported previously[18] provides a framework for considering the molecular orbitals of 2. The bound dtca ligand with a three-coordinate carbon requires overlap of the vacant carbon $p_{\perp}$ orbital with filled S, N, and metal orbitals. Detection of only one isomer of 2, given four potential carbon locations by replacement of dithiocarbamate sulfur sites in 1, is consistent with the invariance of the dtca ligand location in the various isomeric dimers reported. A geometric isomer prediction for 2 follows if one assumes the cis alkyne sulfide geometry of 1 and distributes the two dπ electrons accordingly into d_{xy}. The crucial carbenoid p orbital is then correctly positioned to overlap with a filled metal dπ orbital only when the carbon of the dtca ligand lies in the equatorial plane with the dtca sulfur trans to the terminal sulfide. The two enantiomers illustrated below, indistinguishable by NMR, meet these criteria.





We believe the structure of 2 will reveal such a geometry, and efforts to obtain X-ray quality single crystals are in progress.

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Registry No. 1, 94706-52-2; 2, 94706-53-3; $W(CO)_3(detc)_2$, 94706-54-4; $W(CO)(PhC_2Ph)(detc)_2$, 94799-48-1; $[W(CO)_4I_3]^-$, 45000-04-2; $Mo(S)(HC_2H)(S_2CNH_2)_2$, 94706-55-5; diphenylacetylene, 501-65-5; cyclohexene sulfide, 286-28-2.

Supplementary Material Available: Tables of thermal parameters, complete bond distances, calculated hydrogen positions, and values of observed and calculated structure factors, as Tables VII, VIII, IX, and X, respectively (30 pages). Ordering information is given on any current masthead page.

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