Conversion of a Dithiocarbamate Ligand to a Thiocarboxamido Ligand To Form W(S)(PhC≡CPh)(S_2CNEt_2)($SCNEt_2$)

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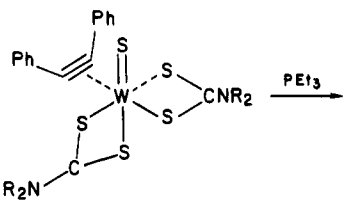
The W(IV) bis(dithiocarbamate) complexes W(S)(PhC≡CPh)(S_2CNR_2)$_2$ (R = CH_3, C_2H_5) lose one sulfur atom when treated with an equivalent of triethylphosphine at −78 °C. The products W(S)(PhC≡CPh)($SCNR_2$)(S_2CNR_2) contain a thiocarboxamido ligand in place of one dithiocarbamate. The molecular structure of the ethyl derivative was determined by a single-crystal X-ray diffraction study (monoclinic, $P2_1/a$; a = 16.927 (6) Å, b = 9.951 (3) Å, c = 17.669 (6) Å, β = 118.49 (3)°, and Z = 4; R = 0.078 and R_w = 0.064 for 1962 reflections with $I > 3\sigma(I)$). The carbenoid carbon of the thiocarboxamido ligand lies cis to the alkyne ligand in the plane defined by the metal–alkyne triangle. The orientation of the η^2-$SCNEt_2$ fragment allows the unique p orbital of the three-coordinate carbon to overlap with the lone filled dπ orbital of the roughly octahedral d^2 tungsten(IV) ion. A dynamic process equilibrates the two dithiocarbamate alkyl substituents on the NMR time scale with an activation barrier of 15.9 kcal/mol. We suggest that this process is promoted by dechelation of the η^2-thiocarboxamido sulfur to generate a fluxional five-coordinate intermediate.

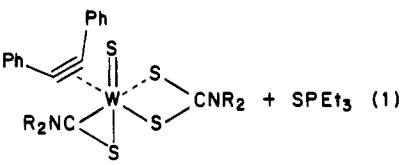
Introduction

The potent nucleophilicity of trialkylphosphines is often utilized in ligand substitution reactions with transition-metal complexes[1] and, less commonly, in reactions of coordinated ligands.[2] We have previously reported that organophosphines promote conversion of a dithiocarbamate ligand to a thiocarboxamido ligand in a reaction which produces a dinuclear molybdenum product.[3] Of course thiocarboxamido metal complexes have been prepared by a variety of methods with oxidative addition of the Cl–C bond in $ClC(S)NR_2$ reagents often the preferred route.[4,5]

Although the major product formed from W(CO)(PhC≡CPh)(S_2CNR_2)$_2$ and cyclohexenyl sulfide is W(S)(PhC≡CPh)(S_2CNR_2)$_2$ (1), a thiocarboxamido W(IV) analogue, W(S)(PhC≡CPh)($SCNR_2$)(S_2CNR_2) (2), was identified as a minor product.[6] We now report that treatment of W(S)(PhC≡CPh)(S_2CNR_2)$_2$ with 1 equiv of triethylphosphine results in sulfur atom abstraction (eq 1) and forms thiocarboxamido complex 2. Equation 1 thus



1a, R = methyl
b, R = ethyl



2a,b

represents a rational synthesis of the W(IV) alkyne derivative 2. The molecular structure and dynamic NMR properties of W(S)(PhC≡CPh)($SCNR_2$)(S_2CNR_2) are presented and discussed in this paper.

The molecular orbital scheme used to rationalize the observed structure of the molybdenum dimer 3 serves as a point of departure for understanding the bonding and geometry of the two isolated monomers 1 and 2.[3] Note that 1 and 2 are tungsten analogues of the molybdenum fragments which would result if one could carry out the imaginary cleavage of dimer 3 into monomers with each segment retaining both the alkyne and sulfide of the original bridged dinuclear compound.

Experimental Section

Methylene chloride (Fisher) was dried over calcium hydride and distilled under purified nitrogen before use. W(S)(PhC≡CPh)(S_2CNEt_2)$_2$ was prepared as previously described;[6] the *N,N*-dimethyl derivative is synthesized in the same manner. Other reagents and solvents were obtained from commercial sources and used as received. IR spectra were recorded with a Beckman 4250 spectrophotometer and were calibrated with polystyrene. NMR spectra were obtained on a Bruker WM250 spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

The preparation of the *N,N*-dimethylthiocarboxamido complex, a compound not previously reported, is described below; the ethyl derivative may be synthesized in the same manner in improved

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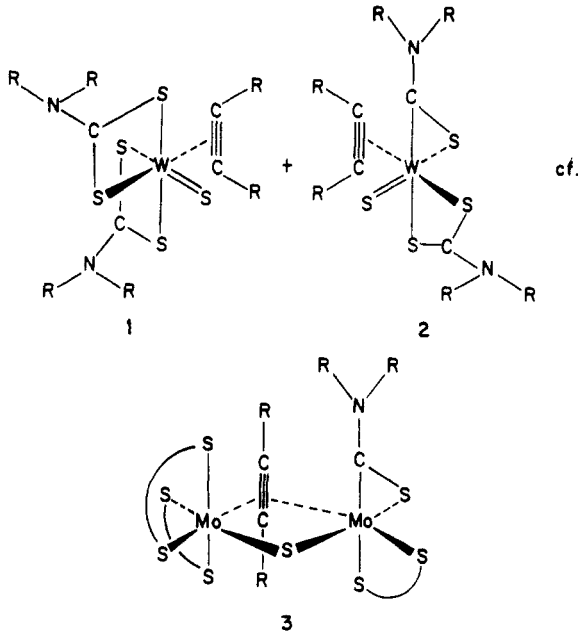

yield relative to the previous method.[6]

W(S)(PhC≡CPh)(SCNMe$_2$)(S$_2$CNMe$_2$) (2a). A 25-mL Schlenk tube was charged with 0.55 g of W(S)(PhC≡CPh)(S$_2$CNMe$_2$)$_2$ (0.80 mmol). The tube was capped with a rubber septum and purged with nitrogen gas. Methylene chloride (8 mL) was syringed into the system while a nitrogen blanket was maintained. The solution was cooled to −78 °C, and an equivalent of triethylphosphine was added as a solution in methylene chloride. The solution was stirred for 90 min and then permitted to warm slowly to room temperature. Following solvent removal under vacuum, no further precautions were taken against atmospheric oxygen. The residue was dissolved in a minimum of toluene and chromatographed on a Florisil column with toluene as the eluent. The bright yellow powder obtained after evaporation of the toluene and trituration with hexanes weighed 0.25 g (50% yield). The product W(S)(PhC≡CPh)(S$_2$CNMe$_2$)(SCNMe$_2$) was readily crystallized from methylene chloride/hexanes at −20 °C as red-orange blocks: IR (KBr) 1558, 1525 (C—N), 492 (W=S), other absorptions 1391 (s), 1150 (s) cm^{-1}; NMR ($CDCl_3$) δ 7.80–7.10 (m, 10 H, phenyl), 3.80 (s, sharp, 3 H, SCNMe$_2$), 3.45 (s, br, 3 H, S$_2$CNMe$_2$), 3.43 (s, sharp, 3 H, SCNMe$_2$), 3.32 (s, br, 3 H, S$_2$CNMe$_2$). Anal. Calcd for $WS_4N_2C_{20}H_{22}$: H, 3.68; C, 39.87; S, 21.28. Found: H, 3.83; C, 39.69, S, 21.47.

W(DCNE)(PhC≡CPh)(S$_2$CNMe$_2$)$_2$. A 100-mL Schlenk flask was flushed with nitrogen gas and charged with 0.22 g of W(S)(PhC≡CPh)(S$_2$CNMe$_2$)$_2$ (0.35 mmol) and 15 mL of CH_2Cl_2. To the solution was added 0.50 g of *trans*-dicyanoethylene (DCNE, 6.4 mmol), and the solution was cooled to −78 °C. A methylene chloride solution of triethylphosphine (0.04 g, approximately 0.3 mmol) was slowly syringed into the solution. The system was stirred for 1 h before it was permitted to warm slowly to room temperature and stirred for an additional hour. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a Florisil column with 1:2 diethyl ether/methylene chloride as the eluent. A yellow band eluted first, identified as DCNE: mp 93–95 °C (lit.[7a] mp 96.8 °C); IR (KBr) 3060 (CH), 2240 (CN) cm^{-1} (lit.[7b] 2240 (CN) cm^{-1}). The second, orange band was reduced to an oil and crystallized from methylene chloride/hexanes, giving 0.12 g (51%) of W(DCNE)(PhC≡CPh)(S$_2$CNR$_2$)$_2$:[8] IR (KBr) 2200 (sharp, nitrile CN), 1520 (br, dithiocarbamate CN) cm^{-1}; NMR ($CDCl_3$) δ 7.8–7.4 (m, 10, phenyl), 3.39, 3.29, 3.22, 3.10 (s, 3 H each, S$_2$CNMe$_2$), 2.97 (d, 1 H, J = 9.2 Hz), 1.61 (d, 1 H, J = 9.2 Hz, olefinic H).

Collection of Diffraction Data. Crystals of W(S)(PhC≡CPh)(S$_2$CNEt$_2$)(SCNEt$_2$) suitable for the X-ray diffraction study were grown by slow evaporation of a methylene chloride/hexanes solution. An orange prism having approximate dimensions 0.20 × 0.40 × 0.35 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[9a] A monoclinic cell was indicated from 25 centered reflections found in the region 20° < 2θ < 26° and refined by least-squares calculations. The cell parameters are listed in Table I.

Table I. Crystallographic Data for W(S)(PhC≡CPh)(S$_2$CN(CH$_2$CH$_3$)$_2$)(SCN(CH$_2$CH$_3$)$_2$)

Crystal Data	
mol formula	$WS_4N_2C_{24}H_{30}$
fw	658.63
space group	$P2_1/a$
cell parameters	
a, Å	16.927 (6)
b, Å	9.951 (3)
c, Å	17.669 (6)
β, deg.	118.49 (3)
V, Å^3	2615.6
ρ(calcd), g/cm^3	1.672
Z	4
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.71073)
linear abs coeff, cm^{-1}	50.0
scan type	$\omega/1.67\theta$
scan width, deg	1.10 + 0.35 tan θ
bkgd	25% of full scan width on both sides
θ limits	$2 \le 2\theta \le 50$
quadrant collected	$+h, +k, +l$
unique data	4589
data with $I > 3\sigma(I)$	1962
R	0.078
R_w	0.064
largest parameter shift	0.27
goodness of fit	2.08

Diffraction data were collected in the quadrant $+h,+k,\pm l$ under the conditions specified in Table I. Three standard reflections chosen as intensity standards were monitored every 5 h and showed no significant (<1.5%) decay. The crystal orientation was checked after every 300 reflections, and recentering was performed if the scattering vectors varied by more than 0.15°. Psi scans with nine reflections having 80° < χ < 90° were performed to provide an empirical correction for absorption. A total of 1962 reflections having $I > 3\sigma(I)$[9b] were used in the solution and refinement of the structure. The data were corrected for Lorentz-polarization effects and absorption during the final stages of refinement.

Solution and Refinement of the Structure. The structure solution was straightforward from the application of the heavy-atom method. The space group $P2_1/a$ was deduced from the systematic absences $h0l$, $h \neq 2n$, and $0k0$, $k \neq 2n$. The tungsten atom was located in a three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were obtained from the subsequent Fourier and difference Fourier calculations.

Least-squares refinement of the 31 non-hydrogen atoms allowing all except the phenyl carbons to vary anisotropically produced unweighted and weighted residuals of 0.084 and 0.073, respectively. The positions of the hydrogen atoms were then calculated by using a C–H distance of 0.95 Å with the isothermal parameter set at 5.0. Further full-matrix least-squares refinement converged with R = 0.78 and R_w = 0.064.[9c] The final difference Fourier map contained three peaks with intensities between 1.0 and 2.1 e/Å^3, all of which were determined to be residual electron density around the tungsten atom.

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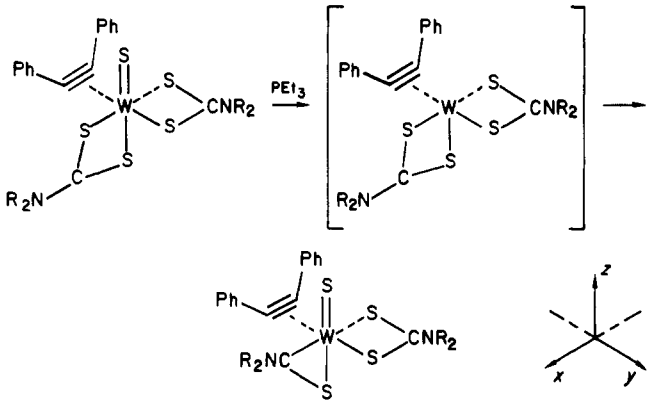
(9) (a) Programs utilized during solution and refinement were from the Enraf-Nonius structure determination package. (b) $I = S(C + RB)$ and $\sigma(I) = \{[2S^2(C + R^2B) + (pI)^2]\}^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background time, B = total background count time and p = 0.01 is a correction factor. (c) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [2F_o/\sigma(R_o^2)]^2$ and $\sigma(F_o^2) = \{[\sigma^2(I) + p^2I^2]\}^{1/2}$ with p assigned a value of 0.01. Expressions for residuals are $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]\}^{1/2}$.

Scheme I



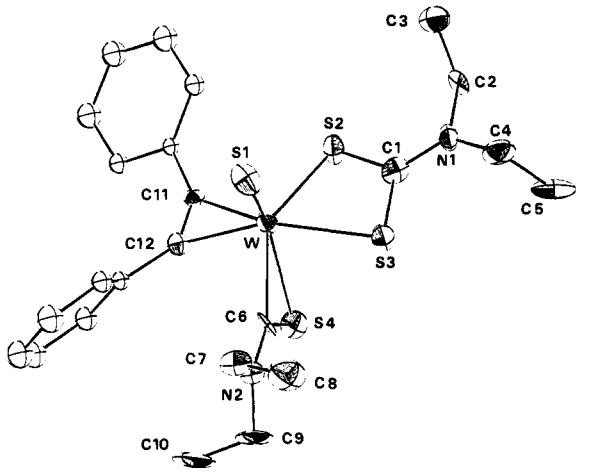


Figure 1. The molecular structure of W(S)(PhC≡CPh)(S_2CNEt_2)($SCNEt_2$) showing the atomic labeling scheme.

Results and Discussion

Syntheses. Triethylphosphine reacts with W(S)(PhC≡CPh)(S_2CNR_2)$_2$ complexes (R = CH_3 (**1a**), C_2H_5 (**1b**)) to generate W(S)(PhC≡CPh)(S_2CNR_2)($SCNR_2$) (**2**) products. Small amounts of other reaction products were separated during chromatography, but these minor byproducts were not characterized. Both IR and NMR spectral data, as well as chromatographic behavior, indicated that the product for R = ethyl, **2b**, was identical with the compound obtained previously as a byproduct in the formation of W(S)(PhC≡CPh)(S_2CNEt_2)$_2$.[6]

Organophosphines are known to abstract metal-bound sulfur atoms.[10-12] Fackler and co-workers, for example, demonstrated that triphenylphosphine preferentially abstracts sulfur from persulfido linkages in Ni(II) dithiocarbamate derivatives.[10] Newton, McDonald, Yamanouchi, and Enemark[11] have shown that triethylphosphine selectively removes a terminally bound sulfur atom from dimeric Mo(V) reagents which also contain bridging sulfurs and dithiocarbamate ligands. Thus, it is likely that the terminal sulfide atom, rather than a dithiocarbamate ligand, is the source of the abstracted sulfur in this study. Direct sulfur abstraction from dithiocarbamate ligands has not yet been observed, and we have previously reported phosphine attack at an alkyne carbon in the presence of dithiocarbamate ligands in W(alkene)(alkyne)(S_2CNR_2)$_2$ complexes.[8] Thus, we favor terminal sulfur atom abstraction as the first step in the formation of the thiocarboxamido complex which is then accessible by internal oxidative addition of a C–S bond (Scheme I).[13] Ample precedent exists for metal-based cleavage of similar C–S bonds.[14]

Additional support for a simple sulfide abstraction mechanism was obtained by adding the triethylphosphine

Table II. Final Positional Parameters and Their Standard Deviations for All Non-Hydrogen Atoms

atom	x	y	z
W	0.07287 (6)	0.0522 (1)	0.22544 (7)
S(1)	0.1457 (4)	0.1725 (8)	0.1794 (4)
S(2)	0.0229 (4)	−0.1539 (7)	0.1405 (4)
S(3)	0.1982 (4)	−0.1243 (7)	0.2859 (4)
S(4)	0.0461 (4)	−0.0423 (9)	0.3517 (4)
N(1)	0.157 (1)	−0.319 (2)	0.169 (1)
N(2)	0.163 (1)	0.162 (2)	0.421 (1)
C(1)	0.131 (1)	−0.211 (3)	0.195 (1)
C(2)	0.91 (1)	−0.401 (2)	0.093 (1)
C(3)	0.082 (2)	−0.346 (3)	0.009 (1)
C(4)	0.257 (2)	−0.357 (3)	0.212 (1)
C(5)	0.281 (1)	−0.474 (3)	0.272 (1)
C(6)	0.110 (1)	0.081 (2)	0.356 (1)
C(7)	0.162 (2)	0.153 (3)	0.500 (1)
C(8)	0.094 (2)	0.241 (4)	0.505 (2)
C(9)	0.225 (2)	0.258 (3)	0.415 (1)
C(10)	0.322 (2)	0.218 (4)	0.454 (2)
C(11)	−0.060 (1)	0.117 (2)	0.160 (1)
C(12)	−0.014 (1)	0.195 (3)	0.221 (1)
C(13)	−0.150 (1)	0.097 (2)	0.079 (1)
C(14)	−0.220 (1)	0.163 (2)	0.079 (1)
C(15)	−0.307 (1)	0.162 (3)	0.001 (1)
C(16)	−0.314 (1)	0.098 (2)	−0.071 (1)
C(17)	−0.242(1)	0.036 (3)	−0.069 (1)
C(18)	−0.159 (1)	0.034 (2)	0.006 (1)
C(19)	−0.022 (1)	0.328 (2)	0.254 (1)
C(20)	0.039 (1)	0.428 (2)	0.261 (1)
C(21)	0.035 (1)	0.550 (3)	0.296 (1)
C(22)	−0.026 (1)	0.569 (3)	0.324 (1)
C(23)	−0.088 (1)	0.478 (2)	0.318 (1)
C(24)	−0.085 (1)	0.355 (2)	0.284 (1)

Table III. Selected Bond Distances (Å)

W–S(1)	2.138 (5)	W–S(2)	2.442 (5)
W–S(3)	2.562 (4)	W–S(4)	2.651 (5)
W–C(6)	2.10 (1)	W–C(11)	2.08 (1)
W–C(12)	2.02 (2)	C(11)–C(12)	1.26 (2)
C(6)–S(4)	1.62 (1)	C(6)–N(2)	1.34 (2)
C(1)–S(3)	1.70 (1)	C(1)–S(2)	1.71 (1)
C(1)–N(1)	1.33 (2)		

Table IV. Selected Interatomic Angles (deg)

S(1)–W–C(6)	114.5 (5)	S(1)–W–S(4)	151.6 (2)
S(1)–W–S(3)	91.7 (1)	S(1)–W–S(2)	109.3 (2)
S(1)–W–C(11)	106.2 (4)	S(1)–W–C(12)	97.8 (4)
C(6)–W–S(4)	37.6 (5)	C(6)–W–S(3)	83.2 (4)
C(6)–W–C(11)	104.5 (6)	C(6)–W–C(12)	77.0 (6)
S(4)–W–S(3)	81.1 (1)	S(4)–W–S(2)	94.0 (1)
S(4)–W–C(11)	90.5 (4)	S(4)–W–C(12)	82.3 (4)
S(3)–W–S(2)	69.9 (1)	S(3)–W–C(11)	87.2 (4)
S(3)–W–C(12)	160.1 (5)	S(2)–W–C(11)	87.2 (4)
S(2)–W–C(12)	122.4 (5)	C(11)–W–C(12)	35.8 (5)
N(2)–C(6)–S(4)	131 (1)	C(12)–C(11)–C(13)	144 (1)
C(11)–C(12)–C(19)	139 (2)		

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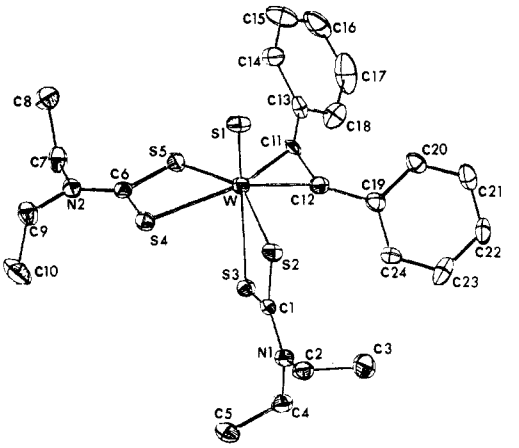

Figure 2. The molecular structure of W(S)(PhC≡CPh)(S_2CNEt_2)$_2$, reproduced from ref 6.

reagent slowly at low temperature to a solution of **1a** containing excess *trans*-dicyanoethylene. The clean formation of W(DCNE)(PhC≡CPh)(S_2CNMe_2)$_2$[8] suggests that the intermediate formed is equivalent to an unsaturated W(PhC≡CH)(S_2CNR_2)$_2$ species in terms of reactivity.

The Molecular Structure of W(S)(PhC≡CPh)(S_2CNEt_2)(SCNEt$_2$). The solid-state structure of (diphenylacetylene)(diethyldithiocarbamato)(diethylthiocarboxamido)sulfidotungsten(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. The diphenylacetylene ligand adopts a normal bent geometry. The two phenyl rings are canted 25.8° and 53.5° relative to the W–C11–C12 plane; the ring proximal to the thiocarboxamido carbon has the larger dihedral angle. Selected bond distances and interatomic angles are listed in Tables III and IV, respectively. The alkyne and the dithiocarbamate lie nearly in the same plane with the tungsten atom, and the thiocarboxamido ligand is approximately perpendicular to this plane. The thiocarboxamido complex is structurally similar to the bis(dithiocarbamate) starting material (Figure 2, reproduced for reference purposes).[6] In particular, both structures show the expected cis orientation of the terminal sulfide ligand and the alkyne.

The observed geometry of the thiocarboxamido complex permits the metal dπ orbitals to utilize the π-donor capabilities of the terminal sulfur and alkyne, while the π-acceptor needs of both the alkyne and the thiocarboxamido carbon are still satisfied. Referring to the coordinate system defined in Scheme I, the terminal sulfide ligand destabilizes metal orbitals d_{xz} and d_{yz} by acting as a π-donor. The alkyne also drives up the energy of d_{yz} through $\pi_\perp$ donation to the metal, and it stabilizes d_{xy} through the $\pi_\parallel$* interaction.[15,16] The thiocarboxamido moiety can satisfy the back-bonding requirement of C6 by aligning the empty carbon p orbital with d_{xy}, since this is the only filled d orbital in this W(IV) system. Thus the geometry of the complex can be rationalized on the basis of frontier orbital π interactions, as predicted in previous work.[6] This is also the geometry of the Mo(S)(RC≡CR)(S_2CNMe_2)(SCNMe$_2$) fragment in the dinuclear molybdenum compound **3**.[3]

The W–C11 distance in **2b** is the same within experimental error as the distance found for the analogous separation in **1b**, while the W–C12 vector is slightly shorter in the thiocarboxamido complex, 2.065 (7) vs. 2.02 (2) Å. The slight slippage of the alkyne toward the thiocarboxamido carbenoid carbon may be due to a three-center, two-electron interaction between these ligands and the metal. Here the metal d_{xy}, alkyne $\pi_\parallel$*, and carbenoid p_y orbitals overlap constructively to generate the filled molecular orbital of this three-center interaction. A similar bonding scheme has been suggested to exist between cis carbonyl and alkyne ligands in d^4 complexes such as Mo(CO)(PhC≡CPh)(PEt_3)$_2$$Br_2$.[17] This weak attractive interaction is also reflected in the angle subtended by the thiocarboxamido carbon and C12, 77.0°, compared to the analogous angle between S2 and C12, 87.5°, found for **1b**. The distance of 2.57 Å between C12 and C6 in **2b** is, however, too long for any significant direct overlap.

The tungsten–terminal sulfide distance in complex **2b** is nearly the same as the corresponding bond length in **1b** (2.138 (5) vs. 2.147 (2) Å, respectively). The thiocarboxamido sulfur atom located trans to the terminal sulfide, 2.65 Å from the tungsten, is more weakly bound than either of the dithiocarbamate sulfur atoms. The high trans influence of the sulfido ligand was also evident in the structure of **1b** where the same W–S distance of 2.65 Å was found for the dithiocarbamate sulfur located trans to the sulfido ligand. The angle subtended by the terminal sulfide ligand and the sulfur atom nominally trans to it is also similar in both structures, 153.7° for the bis(dithiocarbamate) complex and 151.6° for the thiocarboxamido complex. Although the distance from tungsten to S3 (the sulfur atom bound trans to the alkyne) is identical within experimental error in both complexes **1b** and **2b**, sulfur S2 (trans to the thiocarboxamido carbon) is slightly further from the metal than the analogous sulfur in the bis(dithiocarbamate) complex, 2.44 vs. 2.41 Å. This marginal bond lengthening is probably due to the strong trans influence of C6, which can be viewed as a metal-bound carbene.[18] The W–S3 distance of 2.56 Å needs to be mentioned here to highlight the high trans influence of the alkyne relative to the thiocarboxamido carbon. The W–C bond length of 2.10 Å to the thiocarboxamido carbon suggests some multiple-bond character between these atoms.[19] This distance is similar to other tungsten–carbon linkages in this class[20] with $(OC)_5W$=CPh_2 representative of the longer tungsten–carbene bond lengths (2.15 Å)[20d] and (dmpe)(Me_3CCH_2)(Me_3CC)W=CHCMe$_3$ exemplify-

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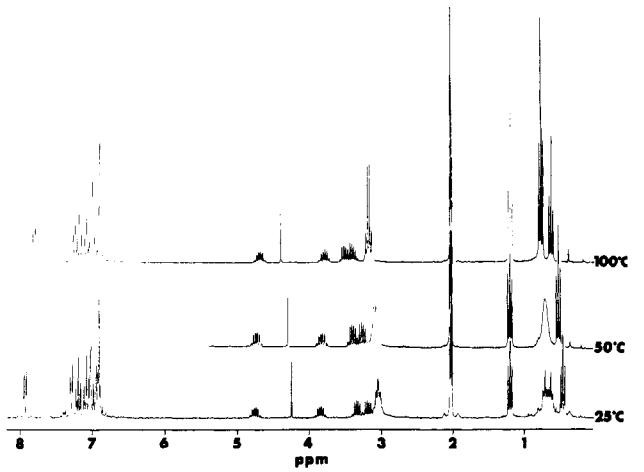

Figure 3. Variable-temperature proton NMR spectrum of **2b**.

ing the shorter W–C double bonds (1.94 Å).[20e]

Spectroscopic Behavior. The infrared spectrum of the *N,N*-dimethyl derivative **2a** is very similar to the spectrum for the ethyl derivative, which has been discussed in detail previously.[6] The presence of two absorption bands in the C–N region is associated with the formation of the thiocarboxamido linkage. The ν (W=S) mode absorbs in the expected frequency region at 492 cm^{-1}.

An interesting feature of the NMR spectrum of the *N,N*-dimethyl complex **2a** is the broadness at room temperature of two methyl resonances (peak width at half-height is about 0.2 ppm). A similar phenomenon is observed for the ethyl derivative in deuteriotoluene solvent (Figure 3). The ambient temperature spectrum in Figure 3 is the same as previously described,[6] though the chemical shifts are different because of the change in solvent. All proton resonances are sharp except for those assigned to the dithiocarbamate ligand. Two overlapping multiplets at δ 0.55 are observed for the methyl groups of the S_2CNEt_2 moiety, and a multiplet at δ 3.0 is assigned to the methylenes. The two methyl signals assigned to the dithiocarbamate ligand of **2b** coalesce near 50 °C, and they sharpen into a triplet at high temperatures. The dithiocarbamate methylene protons undergo similar changes, becoming a single quartet a high temperature. The free energy of activation for this process is 15.9 kcal/mol (calculated for methyl exchange from the rate constant at the coalescence temperature: $k = \pi(\Delta\nu_{AB})/(2^{1/2})$ at T_c). Similar fluxional behavior has been observed by Dean in the proton NMR spectrum of $Fe(CO)_2(S_2CNMe_2)(SCNMe_2)$ at room temperature.[14d]

For the bis(dithiocarbamate) complex it was suggested[6] that the sulfur atom trans to the terminal sulfide could be labile and that dissociating it could initiate the fluxional process which averages the dithiocarbamate protons and the alkyne protons. It is possible that the thiocarboxamido sulfur is also labile, permitting the thiocarboxamido ligand to switch from a bidentate to a monodentate coordination mode. Such a fluxional five-coordinate intermediate would exchange only the dithiocarbamate alkyl groups with one another since the thiocarboxamido alkyl groups are fixed uniquely in the ground-state isomer. Note that as long as the chelating ligands remain planar, the environments of the alkyl groups correlate with the metal-bound atoms. Thus C6 and S4 return respectively to equatorial and axial positions in the ground state after any fluxional process, while S2 or S3 can occupy either coordination site of the dithiocarbamate equally well. The observed barrier of 15.9 kcal/mol is well below typical values reported for dithiocarbamate C–N bond rotations in related systems.[21] Thus we see no reason to invoke rotation around the dithiocarbamate C1–N1 bond, but neither can we definitely rule out this possibility.

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Registry No. **1a**, 101519-39-5; **2a**, 101519-38-4; **2b**, 94706-53-3; $W(DCNE)(PhC{\equiv}CPh)(S_2CNMe_2)_2$, 98735-68-3.

Supplementary Material Available: Tables of thermal parameters, complete bond distances and angles, calculated hydrogen positions, and values of observed and calculated structure factors (Tables V–IX) (20 pages). Ordering information is given on any current masthead page.

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