Transformations Leading to the Generation of Dithiolene Ligands Initiated by Reactions of Sulfur-Rich $WS(S_2)(S_2CNR_2)_2$ Complexes with Dimethyl Acetylenedicarboxylate and Phenylacetylene

Patrick J. Lim, Vernon C. Cook, Christian J. Doonan, and Charles G. Young*

School of Chemistry, University of Melbourne, Victoria 3010, Australia

Edward R. T. Tiekink

Department of Chemistry, University of Adelaide, Adelaide, South Australia 5005, Australia

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Purple $W(S_2C_2R'_2)\{SC(R')C(R')SC(NR_2)S\}(S_2CNR_2)$ (**1**, donor atoms italicized) are formed in the reactions of $WS(S_2)(S_2CNR_2)_2$ (R = Me, Et) with dimethyl acetylenedicarboxylate (DMAC, R′ = CO_2Me) in dichloromethane at room temperature or phenylacetylene (R′ = Ph/H) in refluxing 1,2-dichloroethane. These complexes undergo CS−C(NR_2) bond cleavage upon photolysis to produce green thiocarboxamido species, $W(S_2C_2R'_2)_2(S_2CNR_2)(SCNR_2)$ (**2**), which in turn convert to orange, anionic, bis(dithiolene) complexes, $[W(S_2C_2R'_2)_2(S_2CNR_2)]^-$ (**3**, isolated as various tetraalkylammonium salts). The complexes have been characterized by microanalysis, IR, UV−visible, and ^1H and ^{13}C NMR spectroscopy. An X-ray crystal structure of **1a**·$0.5H_2O$ (R = Me, R′ = CO_2Me) revealed two independent, pseudo-enantiomeric, eight-coordinate complexes containing novel κ^4-*SC*(R′)*C*(R′)SC(NR_2)*S*$^-$ and bidentate dithiolene and dithiocarbamate ligands. Complexes **2** are fluxional at room temperature and exhibit IR and ^{13}C NMR signals characteristic of thiocarboxamido (ν 1590 cm^{-1}, δ 226−228), dithiocarbamate (ν 1540 cm^{-1}, δ 190−201), and dithiolene ligands. An X-ray crystal structure of NEt_4[**3a**] (R = Me, R′ = CO_2Me) revealed an S_6-donor, trigonal-prismatic anion possessing bidentate dithiocarbamate and dithiolene ligands. In the sequence of transformations, $WS(S_2)(S_2CNR_2)_2$→**1**→**2**→**3**, the construction of two dithiolene ligands from two alkyne units and three chemically distinct sulfur-donor ligands (thio, disulfido, dithiocarbamate) has been tracked for the first time.

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Introduction

Alkyne and 1,1-dithioate moieties are known to participate in metal-assisted fragmentation, rearrangement, and coupling reactions leading to the formation of novel organosulfur complexes.[1−6] These and related reactions, as well as the associated C−C and C−S bond-making and -breaking processes, are relevant to many areas of biology and industry, including the synthesis of enzyme models, fine chemicals, bulk industrial chemicals, and petrochemicals, and in the processing of fossil fuels.[7,8] Dithiocarbamates are involved in some striking examples of these reactions. These include (i) reaction of $CpMoCl(F_3CC{\equiv}CCF_3)_2$ with NaS_2CNR_2 to produce ligand-coupled complexes (eq 1) rather than simple metathesis products,[3] (ii) reaction of $Mo(S_2CNR_2)_2(HC{\equiv}CPh)_2$ with HC≡CPh, which results in the incorporation of dithiocarbamate ligand fragments into dithiolene and amidocyclopentadienyl ligands (eq 2),[4] and (iii) reactions of $MoO(S_2)(S_2CNR_2)_2$, $[Mo_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]^{2+}$, or $Mo(S_2)(S_2CNR_2)_3$ with dimethyl acetylenedicarboxylate (DMAC) to produce melded-ligand complexes **A** and **B**, e.g., eq 3.[5,9] The melded ligand in **B** is also observed in 1-thio-2-iminoene complexes produced in the reaction of $Mo(NPh)(S_2)(S_2CNR_2)_2$ with DMAC.[6] Reactions of this type are not restricted to dithiocarbamate *or* monomeric complexes.[10,11]

Dithiolene complexes[12] are frequent products in the reactions of alkynes and 1,1-dithioate species (e.g., eqs

(1) Linford, L.; Raubenheimer, H. G. *Adv. Organomet. Chem.* **1991**, *32*, 1−119.
(2) Davidson, J. L. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 825−895.
(3) Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1987**, 2715−2722.
(4) Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister C.; Prout, C. K. *Inorg. Chem.* **1986**, *25*, 1923−1925.
(5) (a) Young, C. G.; Yan, X. F.; Fox B. L.; Tiekink, E. R. T. *J. Chem. Soc., Chem. Commun.* **1994**, 2579−2581. (b) Lim, P. J.; Gable, R. W.; Young, C. G. *Inorg. Chim. Acta*, in press.
(6) (a) Coffey, T. A.; Forster, G. D.; Hogarth, G. *J. Chem. Soc., Dalton Trans.* **1996**, 183−193. (b) Forster, G. D.; Hogarth, G. *J. Chem. Soc., Dalton Trans.* **1997**, 2305−2307.
(7) *Sulfur−Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology*: Müller, A., Krebs, B., Eds.; Elsevier: Amsterdam, 1984.
(8) *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series No. 653; American Chemical Society: Washington, D.C., 1996.
(9) Meld: *v.* and *n.* Orig US (> 1930) Perhaps from MELT + WELD. A. *v.t.* and *i.* Merge, blend together (Oxford English Dictionary). We have adopted this term to describe the combination of dithiocarbamate and alkyne units to form new organosulfur (melded) ligands characterized by a more intimate blending of ligand fragments than is typical of, for example, simple insertion or coupling reactions.[5]
(10) (a) Adams, H.; Bancroft, M. N.; Morris, M. J. *Chem. Commun.* **1997**, 1445−1446. (b) Adams, H.; Allott, C.; Bancroft, M. N.; Morris, M. J. *J. Chem. Soc., Dalton Trans.* **1998**, 2607−2609, and references therein.
(11) Abbott, A.; Bancroft, M. N.; Morris M. J. *Chem. Commun.* **1998**, 389−390.

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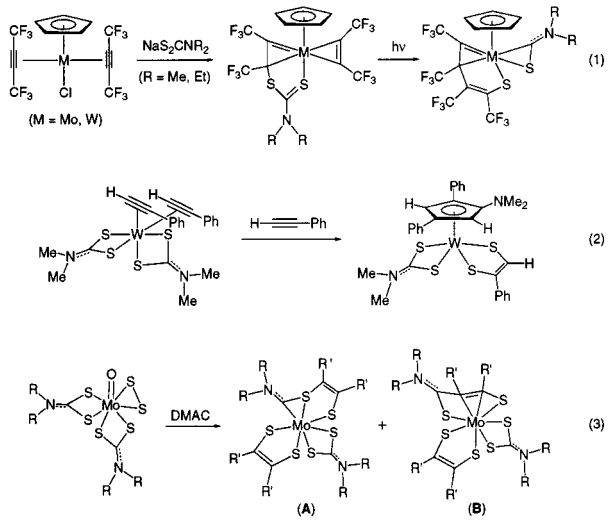
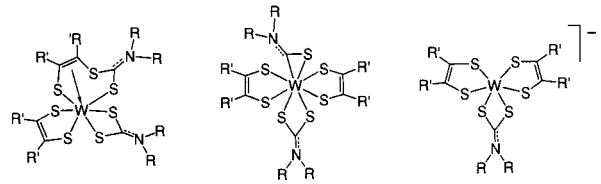


2 and 3). Complexes of this type are important in both biology and industry. In biology, mononuclear Mo and W enzymes exploit a unique pterin−dithiolene ligand (molybdopterin) to anchor and facilitate electron transfer to or from the active sites.[13−15] In industry, maleonitriledithiolate (mnt) and 1,3-dithiol-2-thione-4,5-dithiolate complexes are employed as electrical conductors, photosensitizers, mesomorphic liquid crystals, and semi- and superconducting materials.[16−18] Ligand exchange reactions and reactions of alkynes with metal−sulfur compounds are the two most common synthetic approaches to dithiolene complexes.[12,15] Reactions of terminal thio ligands with alkynes to yield dithiolenes are rare; two examples are the generation of Tp*WX(dithiolene)[19] (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) and [Cp*WS(dithiolene)]$^-$ [20] complexes from Tp*WS_2X and [Cp*WS_3]$^-$, respectively. The formation of dithiolenes via intermediate ligand-coupled or melded-ligand complexes has not been reported.

Here, we describe the sequence of reactions leading to the transformation of $WS(S_2)(S_2CNR_2)_2$[21] into bis(dithiolene) complexes according to the net reaction in eq 4. The sequence is initiated by the reaction of $WS(S_2)(S_2CNR_2)_2$ with the alkynes DMAC or PhC≡CH to produce purple complexes, **1**. These feature novel κ^4-*SC*(R′)*C*(R′)SC(NR$_2$)*S*$^-$ ligands, generated by the coupling of a sulfur atom and a dithiocarbamate ligand by one alkyne, as well as a dithiolene ligand formed from a second alkyne. Irradiation of **1** leads to CS−C(NR$_2$) bond cleavage and the transformation of the κ^4 ligand into dithiolene and thiocarboxamide units, with the formation of green **2**. In the final step of the sequence, **2** are converted into orange, trigonal-prismatic, bis(dithiolene) complexes, **3**. The sequence of reactions reveals the steps involved in the construction of two dithiolene ligands from the three chemically distinct sulfur-donor ligands of $WS(S_2)(S_2CNR_2)_2$. Alternative syntheses for $WO(S_2)(S_2CNEt_2)_2$[22] are also reported.

$$WS(S_2)(S_2CNR_2)_2 + 2R'C{\equiv}CR' \rightarrow [W(S_2C_2R'_2)_2(S_2CNR_2)]^- + \text{“}[SCNR_2]^+\text{”} \quad (4)$$



1 (purple) **2 (green)** **3 (orange)**

a: R = Me, R′ = CO_2Me, **b:** R = Et, R′ = CO_2Me, **c:** R = Me, R′ = H/Ph, **d:** R = Et, R′ = H/Ph

Results and Discussion

Reactions of $WS(S_2)(S_2CNR_2)_2$ with Alkynes. Reactions of $WS(S_2)(S_2CNR_2)_2$ with excess DMAC or PhC≡CH in chlorinated solvents result in the formation of purple complexes, **1**.[23] The reactions involving DMAC, which produce **1a** and **1b**, proceed smoothly and in high yields at room temperature in dichloromethane. The requirement of higher temperatures (reflux in 1,2-dichloroethane) in the reactions involving PhC≡CH leads to the production of green **2c/d** and orange **3c/d** (vide infra) as byproducts in the syntheses of **1c** and **1d**. The air-stable, diamagnetic complexes may be purified by column chromatography and are soluble in

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(12) (a) McCleverty, J. A. *Prog. Inorg. Chem.* **1969**, *10*, 49−221. (b) Mueller-Westerhoff, U. T.; Vance, B. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, Chapter 16.5, pp 595−631. (c) Collison, D.; Garner, C. D.; Joule, J. A. *Chem. Soc. Rev.* **1996**, *25*, 25−32.

(13) (a) *Molybdenum Enzymes, Cofactors, and Model Systems*; Stiefel, E. I., Coucouvanis, D., Newton, W. E., Eds.; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993. (b) Enemark, J. H.; Young, C. G. *Adv. Inorg. Chem.* **1993**, *40*, 1−88. (c) Hille, R. *Chem. Rev.* **1996**, *96*, 2757−2816. (d) Pilato, R. S.; Stiefel, E. I. In *Bioinorganic Catalysis*: Reedijk, J., Bouwman, E., Eds.; Dekker: New York, 1999; pp 81−152.

(14) (a) Kletzin, A.; Adams, M. W. W. *FEMS Microbiol. Rev.* **1996**, *18*, 5−63. (b) Johnson, M. K.; Rees, D. C.; Adams, M. W. W. *Chem. Rev.* **1996**, *96*, 2817−2839.

(15) For models of dithiolenic enzyme centers see the following and references therein: (a) Das, S. K.; Chaudhury, P. K.; Biswas, D.; Sarkar, S. *J. Am. Chem. Soc.* **1994**, *116*, 9061−9070. (b) Oku, H.; Ueyama, N.; Nakamura, A. *Inorg. Chem.* **1997**, *36*, 1504−1516. (c) Lorber, C.; Donahue, J. P.; Goddard, C. A.; Nordlander, E.; Holm, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 8102−8112. (d) Donahue, J. P.; Goldsmith, C. R.; Nadiminti, U.; Holm, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 12869−12881.

(16) (a) Kisch, H. *Coord. Chem. Rev.* **1993**, *125*, 155−172. (b) Benedix, R.; Hofbauer, M.; Möbius, M.; Knoch, F. *Inorg. Chim. Acta* **1997**, *262*, 177−185.

(17) (a) Giroud, A.-M. *Ann. Phys.* **1978**, *3*, 147−149. (b) Giroud, A.-M.; Nazzal, A.; Mueller-Westerhoff, U. T. *Mol. Cryst., Liq. Cryst.* **1980**, *56*, 225−228. (c) Mueller-Westerhoff, U. T.; Nazzal, A.; Cox, R. J.; Giroud, A.-M. *Mol. Cryst., Liq. Cryst.* **1980**, *56*, 249−255. (d) Cortrait, M.; Gaultier, J.; Polycarpe, C.; Giroud, A. M.; Mueller-Westerhoff, U. T. *Acta Crystallogr.* **1983**, *C39*, 833−835. (e) Veber, M.; Fugnitto, R.; Strzelecka, H. *Mol. Cryst., Liq. Cryst.* **1983**, *96*, 221−227.

(18) (a) Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayashi, A.; Clark, R. A.; Underhill, A. E. *Coord. Chem. Rev.* **1991**, *110*, 115−160. (b) Olk, R.-M.; Olk, B.; Dietzsch, W.; Kirmse, R.; Hoyer, E. *Coord. Chem. Rev.* **1992**, *117*, 99−131. (c) Pullen, A. E.; Olk, R.-M. *Coord. Chem. Rev.* **1999**, *188*, 211−262. (d) Jourdain, I. V.; Fourmigue, M.; Guyon, F.; Amaudrut, J. *Organometallics* **1999**, *18*, 1834−1839.

(19) (a) Eagle, A. A.; Harben, S. M.; Tiekink, E. R. T.; Young, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 9749−9750. (b) Eagle, A. A.; George, G. N.; Tiekink, E. R. T.; Young, C. G. *J. Inorg. Biochem.* **1999**, *76*, 39−45.

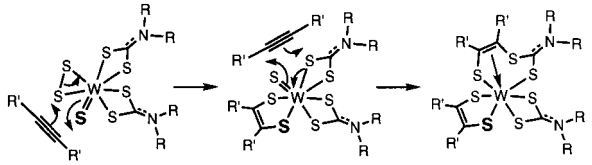
(20) (a) Kawaguchi, H.; Tatsumi, K. *J. Am. Chem. Soc.* **1995**, *117*, 3885−3886. (b) Kawaguchi, H.; Yamada, K.; Lang, J.-P.; Tatsumi, K. *J. Am. Chem. Soc.* **1997**, *119*, 10346−10358.

(21) Pan, W.-H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1985**, 927−929.

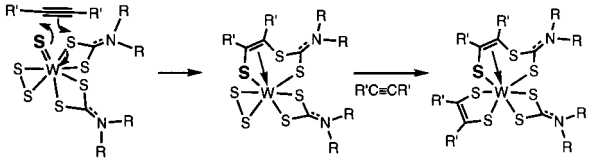
(22) Broomhead, J. A.; Enemark, J. H.; Hammer, B.; Ortega, R. B.; Pienkowski, W. *Aust. J. Chem.* **1987**, *40*, 381−385.

(23) Not all alkynes react with $WS(S_2)(S_2CNR_2)_2$ to produce **1**. For example, PhC≡CPh reacts with $WS(S_2)(S_2CNMe_2)_2$ to produce blue $W_2(\mu\text{-}S_2)(\mu\text{-}S)(S_2C_2Ph_2)_2(S_2CNMe_2)_2$, which has a structure resembling that of $Mo_2(\mu\text{-}S_2)(\mu\text{-}S)\{N(2,6\text{-}^iPr_2C_6H_3)\}_2(S_2CNEt_2)_2$ (see: Coffey, T. A.; Hogarth, G. *Polyhedron* **1997**, *16*, 165−169) but with bidentate dithiolene ligands in place of the imido ligands. Lim, P. J. Ph.D. Dissertation, University of Melbourne, 1999.

Scheme 1



Scheme 2



chlorinated solvents, acetonitrile, and *N*,*N*-dimethylformamide but insoluble in alcohols, ethers, and hydrocarbons.

Microanalytical data for **1** were consistent with the general formula "$WS_3(R'C{\equiv}CR')_2(S_2CNR_2)_2$". The incorporation of the alkyne units into dithiolene and κ^4-*SC*(R′)*C*(R′)SC(NR$_2$)*S*$^-$ ligands was established by spectroscopic and crystallographic studies (vide infra). The κ^4 ligand, which originates from the coupling of a sulfur atom and a dithiocarbamate ligand by an alkyne, may be formulated as a monoanionic thia-π-allyl thione; this would demand a formal metal oxidation state of +IV.[24] The mechanisms of the reactions remain uncertain, as available probes (e.g., low-temperature NMR spectroscopy) failed to identify any transient species. While alkynes are known to react with each of the ligands of $WS(S_2)(S_2CNR_2)_2$, they are expected to be most susceptible to nucleophilic attack by the terminal thio or disulfido ligands. A central role for the thio ligand is consistent with the failure of $WO(S_2)(S_2CNEt_2)_2$[22] and $WO(S_2)_2$(bpy) (bpy = 2,2′-bipyridine)[25] to react with DMAC or phenylacetylene, even at high temperatures (>90 °C). Formation of **1** may be rationalized by nucleophilic attack of the thio ligand on the alkyne triple bond, followed by or in concert with attack on the disulfido (Scheme 1) or dithiocarbamate ligands (Scheme 2). In the mechanism in Scheme 1, initial attack on the alkyne generates a transient vinyl sulfide and activates the disulfido ligand toward electrophilic attack by the β-carbon thereof. This results in S−S bond cleavage, the generation of a dithiolene ligand incorporating the thio-ligand sulfur atom (enlarged and bolded in the schemes), and the formation of a new thio ligand. Subsequent nucleophilic attack by the new thio ligand on a second alkyne leads to the formation of the κ^4 ligand. In Scheme 2, coupling of thio and dithiocarbamate ligands by the alkyne leads to a thia-allyl fragment containing the original thio-ligand sulfur atom. The dithiolene is formed in a separate reaction involving alkyne and disulfido units (the order of these two reactions may be reversed). There is precedent for the generation of dithiolenes from thio and dithiocarbamate ligands, possibly via the κ^4 ligand observed in **1**.[19,20,26]

Infrared (IR) spectra of **1a** and **1b** were dominated by intense bands assignable to the methylcarboxy and dithiocarbamate moieties.[27,28] A weak shoulder (ca. 1600 cm^{-1}) on the ν(C═O) band was tentatively assigned to a ν(C═C) mode associated with the dithiolene or κ^4 ligand. In the IR spectra of **1c** and **1d** a medium intensity absorption around 1592 cm^{-1} was assigned to a ν(C═C) mode of the dithiolene or κ^4 ligands; this band was considerably lower in energy than the ν(C≡C) band of free or π-bonded phenylacetylene.[29,30]

^{1}H and ^{13}C{^{1}H} NMR data are summarized in Table 1. Complete assignments, made possible by gradient heteronuclear multiple quantum coupling (gHMQC) and gradient heteronuclear multiple bond coupling (gHMBC) experiments,[31−34] are given in the Experimental Section. The ^{1}H NMR spectra of **1a** and **1b** exhibited four NR$_2$ methyl resonances and, in the case of **1b**, complex multiplets typical of diastereotopic methylene protons (δ 3.2−4.1). Four singlet methyl resonances in the δ 3.4−4.0 region were assigned to inequivalent methylcarboxy groups. The spectra were clearly indicative of molecular C_1 symmetry, implying the generation of racemic products.

The ^{13}C NMR spectrum of **1a** exhibited 17 resonances, two of the O*C*H$_3$ resonances being accidentally equivalent, while the spectrum of **1b** exhibited the expected 22 resonances. The resonances at ca. δ 82 and 99 featured $^1J_{CW}$ couplings of 5−10 Hz and were assigned to the thia-π-allyl carbons of the κ^4 ligands. Signals around δ 148 and 157 showed no ^{183}W coupling and were assigned to the dithiolene carbon atoms. These assignments are consistent with literature reports. Resonances in the range δ 98−113 are typical of thia-allyl carbon atoms,[10] and resonances at δ 56.2, 71.3, and 73.8 have been assigned to the allyl carbon atoms of the related complex, W{κ^4-*C*H(Me)*C*(H)*C*(Ph)SC(NEt$_2$)*S*}(S$_2$CNEt$_2$)-(CO)$_2$.[35] Dithiolene ^{13}C resonances are consistently

(24) Straightforward bonding descriptions do not apply to complexes of this type. This complicates the assignment of a formal oxidation state and limits its usefulness. Delocalization effects and the assignment of high oxidation states in tungsten dithiolene complexes have been documented elsewhere: (a) Argyropoulos, D.; Lyris, E.; Mitsopoulou, C. A.; Katakis, D. *J. Chem. Soc., Dalton Trans.* **1997**, 615−621. (b) Boyde, S.; Garner, C. D.; Joule, J. A.; Rowe, D. J. *J. Chem. Soc., Chem. Commun.* **1987**, 800−801.

(25) Chakrabarty, P. K.; Bhattacharya, S.; Pierpont, C. G.; Bhattacharyya, R. *Inorg. Chem.* **1992**, *31*, 3573−3577.

(26) The complexes Tp*MS(S$_2$CNEt$_2$) (M = Mo, W) react with DMAC to form Tp*M(S$_2$C$_2$R′$_2$)(SCNEt$_2$-*S*,*C*) complexes. The mechanism of the reactions remains unclear, but the κ^4 ligand found in **1** may form initially, then undergo CS−C bond cleavage (as observed in the **1**→**2** conversions) to yield the observed products. These observations provide indirect support for steps in both Schemes 1 and 2. Lim, P. J. Ph.D. Dissertation, University of Melbourne, 1999.

(27) (a) Gordon, A. J.; Ford, R. A. *The Chemist's Companion: A Handbook of Practical Data, Techniques and References*; Wiley: New York, 1972; pp 211−220. (b) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.

(28) van Gaal, H. L. M.; Diesveld, J. W.; Pijpers, F. W.; van der Linden, J. G. M. *Inorg. Chem.* **1979**, *18*, 3251−3260.

(29) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1−100.

(30) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra, Edition 1*; Aldrich Chemical Co.: Milwaukee, WI, 1985.

(31) Braun, S.; Kalinowski, H.-O.; Berger, S. *100 and More Basic NMR Experiments*; VCH: Weinheim, 1996; pp 308−368.

(32) gHMQC: (a) Hurd, R. E.; John, B. K. *J. Magn. Reson.* **1991**, *91*, 648−653. (b) Ruiz-Cabello, J.; Vuister, G. W.; Moonen, C. T. W.; van Gelderen, P.; Cohen, J. S.; van Zijl, P. C. M. *J. Magn. Reson.* **1992**, *100*, 282−302. (c) Wilker, W.; Leibfritz, D.; Kerssebaum, R.; Bermel, W. *Magn. Reson. Chem.* **1993**, *31*, 287−292.

(33) gHMBC: (a) Müller, L. *J. Am. Chem. Soc.* **1979**, *101*, 4481−4484. (b) Garbow, J. R.; Weitekamp, D. P.; Pines, A. *Chem. Phys. Lett.* **1982**, *93*, 504−509. (c) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093−2094. (d) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH: Weinheim, 1988; pp 267−273.

(34) *Guide to NMR Experiments*, VNMR Version 5.2 Software; Varian Associates: Palo Alto, CA, 1996; p 105.

(35) Asaro, M. F.; Mayr, A.; Kahr, B.; van Engen, D. *Inorg. Chim. Acta* **1994**, *220*, 335−346.

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Table 1. Selected NMR Data[a] for Compounds of Series 1

	^{1}H NMR (δ_H)			^{13}C{^{1}H} NMR (δ_C)								
		κ^4	dithiolene		κ^4 ligand			dithiolene			bidentate	κ^4
compound	OCH_3[b]	=C*H*	=C*H*	OCH_3[b]	*C*=*C*[c]	=*C*H	=*C*Ph	*C*=*C*[c]	=*C*H	=*C*Ph	S_2CNR_2	S_2CNR_2
1a	3.47			53.0	82.9[d]			148.6			200.0	213.5
	3.88			53.1	98.8[d]			156.5				
	3.90			53.4								
	4.01											
1b	3.45			52.9	81.6[d]			148.4			199.1	211.8
	3.87			53.0	98.8[d]			156.7				
	3.89			53.3								
	4.00			54.7								
1c isomer 1[e]		5.57	9.10[g]			68.9	101.1		144.0	157.8	202.4	218.4
1c isomer 2[f]		5.61	8.90[g]			68.7	101.0		139.6	162.9	202.4	218.4
1d isomer 1[e]		5.62	9.09[g]			68.6	101.1		143.9	162.7	201.7	216.7
1d isomer 2[f]		5.66	8.90[g]			68.4	100.9		139.8	157.3	201.7	216.7

[a] In $CDCl_3$ solutions at 285−293 K. [b] Dithiolene and κ^4 groups cannot be distinguished with confidence. [c] C=C of DMAC derivative. [d] Coupling to the metal observed, $^1J_{WC}$ = 5−10 Hz. [e] Major isomer. [f] Minor isomer. [g] Coupling to the metal observed, $^2J_{HW}$ = 7−12 Hz.

observed in the region δ 140−170.[5,6,11,12] The S_2C resonances are in the range expected for dithiocarbamate moieties,[28] the resonance associated with the κ^4 ligand fragment being deshielded relative to that of the bidentate ligand.

The NMR spectra of **1c** and **1d** indicated the presence of two isomers, each having C_1 symmetry. Here, the presence of =CH groups in the κ^4 and dithiolene ligands enhanced structural insights from gHMQC and gHMBC experiments. Thus, the singlet ^{1}H resonances around δ 5.6 correlated with the ^{13}C resonances around δ 68, which were assigned to the =*C*H atoms of the κ^4 ligands. Signals at ca. δ_H 9.0 with $^2J_{HW}$ ca. 8 Hz, correlated with signals at ca. δ_C 140, assigned to the dithiolene =*C*H atoms. Coupling of dithiolene =C*H* protons to NMR-active metal nuclei has been observed in other systems.[36−39] Further, the δ_H 5.6 and 9.0 resonances correlated with the κ^4 ligand =*C*Ph resonances (δ_C ca. 102) and the two dithiolene *C*=*C* resonances (δ_C ca. 160), respectively (Figure 1a,b). Significantly, the δ_H 5.6 resonances also correlated with the *C*NR_2 signal of the κ^4 ligand at δ_C 216 (Figure 1c). The dithiocarbamate S_2CNR_2 signal around δ 202 showed cross-peaks with the methyl (R = Me, **1c**) and methylene (R = Et, **1d**) protons (Figure 1d) but not with the κ^4 ligand resonance at δ_H 5.6. In summary, the δ_H 5.6 and 9.0 =C*H* resonances arise from the κ^4 and dithiolene ligands, respectively. The absence of signals around δ_H 5.6 in **2c** and **2d**, which are devoid of κ^4 ligands, supports these assignments.

Finally, the correlations between the =C*H* and *C*NR_2 signals of the κ^4 ligands suggest that the isomers of **1c** and **1d** differ in the arrangement of the dithiolene ligand substituents, as represented by structures a and b in Figure 2. If complexes containing the alternative orientation of the κ^4 ligand, viz., c in Figure 2, were present, then =C*H* signals devoid of the three-bond $^{13}CNR_2$ correlation would have been observed. Steric interactions between the alkyl and phenyl groups in c may preclude formation of the κ^4-*SC*(H)*C*(Ph)SC(NR_2)-*S*$^-$ ligand.

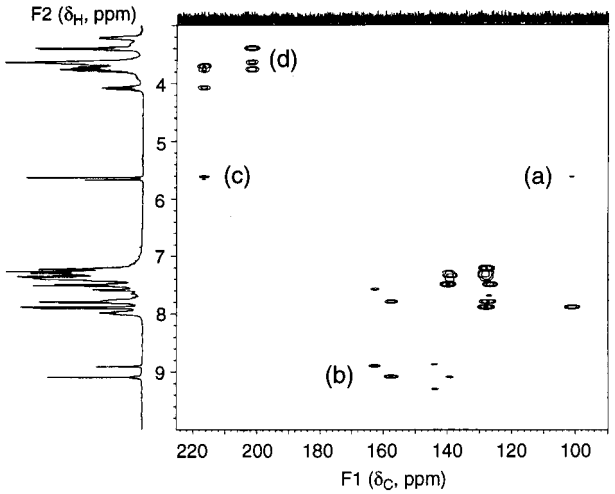

Figure 1. Part of the gHMBC NMR spectrum of **1d** showing the correlations (a−d) discussed in the text.

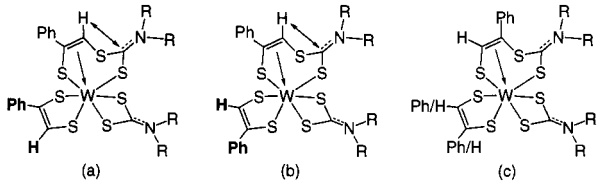

Figure 2. Possible structures for complexes **1c** and **1d**. Isomers a and b differ in the arrangement of the dithiolene H and Ph substituents (bolded). The correlated =C*H* and S_2CNR_2 atoms of the κ^4 ligand are connected by arrows; isomers c would not exhibit the correlation.

Purple, dichloromethane solutions of **1a** and **1b** absorb strongly at 413 (shoulder), 510, and 610 nm (shoulder). Solutions of **1c** and **1d** exhibit two distinct absorption bands around 530 and 660 nm, as well as an intense shoulder at 390 nm. These bands are assigned to ligand $\pi-\pi^*$ or ligand-to-metal charge transfer transitions, although the band at 390 nm may be a charge transfer to solvent transition.[40] The electronic spectra are quite different from those of bis(dithiolene) complexes, which normally exhibit broad, intense, long wavelength (λ > 700 nm) transitions (vide infra).[12,40−42]

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(36) Argyropoulos, D.; Mitsopoulou, C.-A.; Katakis, D. *Inorg. Chem.* **1996**, *35*, 5549−5554.
(37) Davies, E. S.; Aston, G. M.; Beddoes, R. L.; Collison, D.; Dinsmore, A.; Docrat, A.; Joule, J. A.; Wilson, C. R.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1998**, 3647−3656.
(38) Whalley, A. L.; Collison, D.; Garner, C. D.; Helliwell, M. *J. Inorg. Biochem.* **1999**, *74*, 337.
(39) Keefer, C. E.; Bereman, R. D.; Purrington, S. T.; Knight, B. W.; Boyle, P. D. *Inorg. Chem.* **1999**, *38*, 2294−2302.
(40) Vogler, A.; Kunkely, H. *Inorg. Chem.* **1982**, *21*, 1172−1175.

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Published on December 1, 2000 on http://pubs.acs.org | doi: 10.1021/om0006561

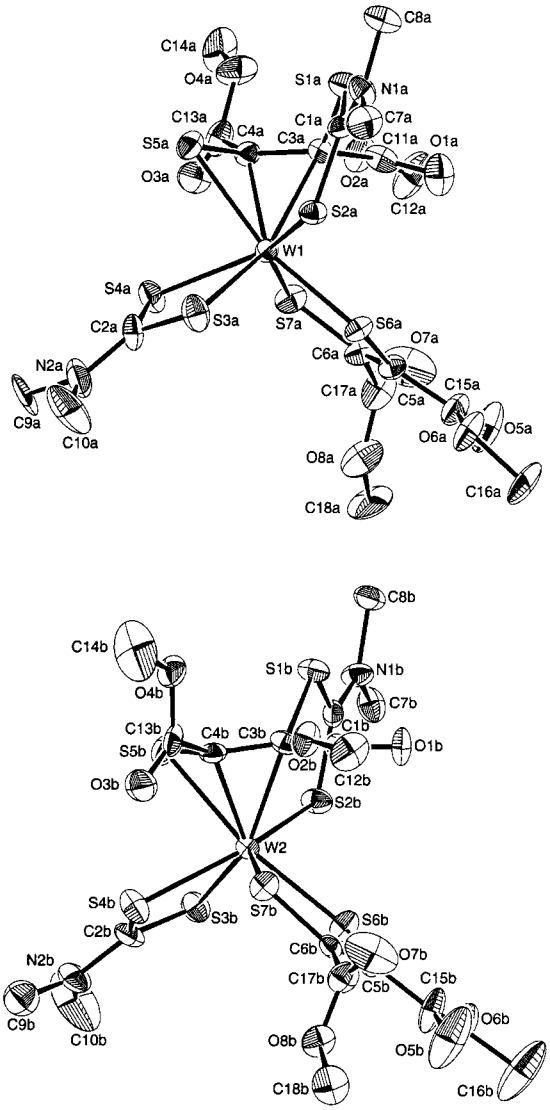

Figure 3. Molecular structures and atom-numbering schemes for molecules a (top) and b (bottom) of **1a**.

Molecular Structure of 1a. Crystals of **1a**·0.5H_2O are composed of two independent molecules (a and b) of **1a** and lattice water molecules; the latter are separated by 2.58(3) Å and aggregated along the *a*-axis. The two molecules of **1a** are pseudo-enantiomeric, the slight deviation from a strict mirror-image relationship (principally in the positioning of the dithiolene and dithiocarbamate ligands) being ascribed to crystal packing forces. Both molecules exhibit a severely distorted eight-coordinate structure as shown in Figure 3. A novel κ^4-*SC*(R′)*C*(R′)SC(NMe_2)*S*$^-$ ligand (see Figures 3 and 4a) and bidentate dithiolene and dithiocarbamate ligands coordinate the tungsten centers. The coordination spheres can be described in terms of a distorted trigonal-prismatic geometry when the thia-π-allyl group is assumed to occupy a single coordination site (Figure 4b). Selected bond distances and angles for both independent molecules are presented in Table 2.

The W−S distances range from 2.364(4) to 2.564(6) Å, the shorter distances being associated with the dithiolene ligands. There is considerable disparity in the W−S(3) and W−S(4) distances in the two molecules, those of molecule b being shorter (av 2.485(4) Å) than those of molecule a (2.510(6) and 2.564(6) Å, respectively). The W−S distances of the κ^4 ligand are equivalent in molecule a (av 2.501(3) Å) but not in molecule b (W(2)−S(2b) = 2.536(4) Å, W(2)−S(5b) = 2.486(4) Å); the opposite applies to the dithiocarbamate W−S distances. Inequivalent W−S(dithiolene) bond distances are observed, W−S(6) (av 2.367(3) Å) being shorter than W−S(7) (av 2.409(2) Å). The C(3)−C(4) fragments are coordinated asymmetrically, the relatively large errors associated with the parameters notwithstanding, with W−C(3) slightly longer than W−C(4); both are typical of W−C distances in allyl complexes.[44]

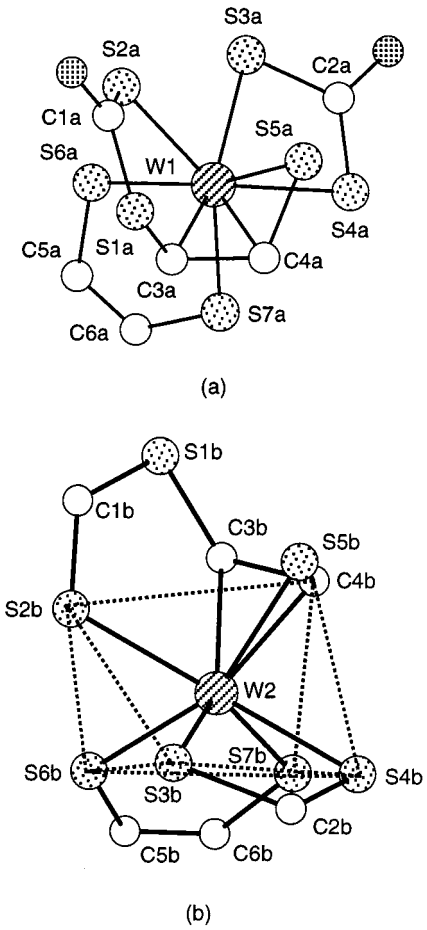

Figure 4. (a) View of molecule a of **1a** looking down on the κ^4 ligand. (b) The very distorted bicapped trigonal prismatic coordination sphere of molecule b of **1a**. Only the metal and ligand framework atoms are shown.

The C(3)−C(4) distances of the κ^4 ligands (1.39(2) and 1.47(2) Å) are comparable with those observed in the dithiolene ligands (1.35(2) Å) and consistent with bond distances in allyl complexes.[44] The S(5)−C(4) distances of 1.74(2) and 1.75(2) Å are intermediate between those of single (1.82 Å) and double (1.61 Å) bonded S−C units.[45] There is evidence that the C−S bond distances of the dithiocarbamate fragment in the κ^4 ligand are

(41) Herman, Z. S.; Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T.; Nazzal, A.; Zerner, M. C. *Inorg. Chem.* **1982**, *21*, 46−56.
(42) Vogler, A.; Kunkely, H.; Hlavatsch, J.; Merz, A. *Inorg. Chem.* **1984**, *23*, 506−509.
(43) (a) Schrauzer, G. N.; Mayweg, V. P. *J. Am. Chem. Soc.* **1965**, *87*, 3585−3592. (b) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, *2*, 72−80.
(44) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.
(45) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

Table 2. Selected Bond Distances and Angles for the Two Independent Molecules of 1a[a]

distance (Å)	molecule a	molecule b	angle (deg)	molecule a	molecule b
W−S(2)	2.507(4)	2.536(4)	W−S(2)−C(1)	108.5(6)	111.2(5)
W−S(3)	2.510(6)	2.489(5)	W−S(3)−C(2)	89.8(7)	87.5(7)
W−S(4)	2.564(6)	2.480(6)	W−S(4)−C(2)	89.3(8)	87.9(7)
W−S(5)	2.495(4)	2.486(4)	W−S(5)−C(4)	58.2(5)	58.5(5)
W−S(6)	2.364(4)	2.369(4)	W−S(6)−C(5)	111.1(6)	112.3(6)
W−S(7)	2.401(3)	2.417(3)	W−S(7)−C(6)	110.6(5)	109.6(4)
W−C(3)	2.25(2)	2.27(2)	W−C(3)−S(1)	119.7(9)	121.9(7)
W−C(4)	2.16(2)	2.17(2)	W−C(4)−S(5)	78.7(7)	78.1(6)
S(1)−C(1)	1.74(2)	1.77(2)	S(2)−W−S(5)	84.0(1)	85.3(1)
S(1)−C(3)	1.81(2)	1.83(2)	S(2)−W−C(3)	82.2(4)	79.2(4)
S(2)−C(1)	1.72(2)	1.69(2)	S(2)−W−C(4)	105.4(4)	103.2(4)
S(3)−C(2)	1.74(2)	1.69(2)	S(3)−W−S(4)	68.2(2)	69.7(2)
S(4)−C(2)	1.68(2)	1.68(2)	S(5)−W−C(3)	68.4(4)	66.8(5)
S(5)−C(4)	1.74(2)	1.75(2)	S(5)−W−C(4)	43.0(4)	43.4(4)
S(6)−C(5)	1.73(1)	1.70(1)	S(6)−W−S(7)	79.4(1)	78.7(1)
S(7)−C(6)	1.69(2)	1.70(1)	C(3)−W−C(4)	38.7(6)	36.3(6)
C(1)−N(1)	1.27(2)	1.30(2)	S(1)−C(1)−S(2)	121(1)	119.5(8)
C(2)−N(2)	1.37(3)	1.38(3)	S(3)−C(2)−S(4)	112(1)	114(1)
C(3)−C(4)	1.47(2)	1.39(2)	S(6)−C(5)−C(6)	118(1)	117(1)
C(5)−C(6)	1.37(2)	1.35(2)	S(7)−C(6)−C(5)	119(1)	121(1)

[a] For molecule a, W = W(1) and other atom numbers are qualified by an a, viz., S(1) = S(1a). For molecule b, W = W(2) and other atom numbers are qualified by a b, viz., S(1) = S(1b). See Figure 3.

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inequivalent, S(2)−C(1) being marginally shorter than S(1)−C(1) in both molecules. This may account for the lengthening of the W−S(2) bond and, in turn, the shortening of the W−S(4) bond trans to it. The same observation is true of related melded-ligand complexes.[6,7] The C(3)−C(4) and S(5)−C(4) distances are shorter and longer, respectively, than C−C and S−C bonds in structurally characterized thia-σ-allyl complexes,[46] consistent with thia-π-allyl coordination.

The κ^4 ligand adopts a relatively "closed" structure characterized by an average S(2)−W−S(5) angle of only 84.7(1)°. The separation between S(1) and S(5) is only about 3.2 Å, and the S(1)−C(3)−C(4) and S(5)−C(4)−C(3) angles are 119(1)° and 113(1)°, respectively, for both molecules. The dihedral angles between the following planes are as indicated: S(1)−C(1)−S(2) and S(2)−W−C(3), 14.4°; S(1)−C(1)−S(2) and C(3)−W−C(4), 56.6°; S(5)−W−C(4) and C(3)−W−C(4), 118.0°. In contrast, an "open" structure is adopted by the melded ligand in **B** (S−Mo−S = 124.2(1)°).[6] The allyldithiocarbamate ligand in W{κ^4-*C*H(Me)*C*(H)*C*(Ph)SC(NEt$_2$)*S*}(S$_2$CNEt$_2$)(CO)$_2$ is closely related to the κ^4 ligands in **1**; it also adopts an "open" structure with a corresponding C−W−S angle of 112.1(3)°.[35]

Fragmentation of the κ^4 Ligand. In solution, purple **1** transform into green **2** upon irradiation with sunlight. Spectral studies revealed the photoisomerizations were clean, quantitative, and irreversible. For example, isosbestic points at 380, 460, and 560 nm were observed for the conversion of **1a** (λ_{max} 510 nm) to **2a** (λ_{max} 680 and 415 nm), as shown in Figure 5a (spectra recorded for the R′ = Ph/H derivatives exhibited isosbestic points at 340, 410, 470, and 580 nm). Conversion of **1** to **2** involves the scission of the CS−C(NR$_2$) bond of the κ^4 ligand with concomitant formation of dithiolene and thiocarboxamido ligands. The decomposition of these and closely related melded ligands to form dithiolene ligands is unprecedented, although different isomerizations involving melded-ligand complexes have been observed by Davidson[3] and Young[5] and co-workers.

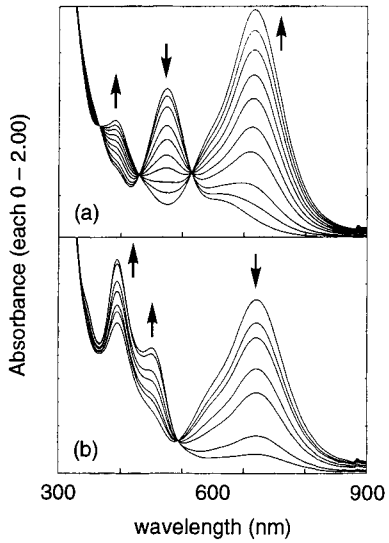

Figure 5. UV−visible spectral changes observed during the transformations **1a**→**2a** (top) and **2b**→**3b** (bottom).

However, it is possible that melded-ligand and related complexes are previously unrecognized intermediates in the generation of dithiolene complexes upon reaction of alkyne and 1,1-dithioate moieties at metal centers (e.g., in eq 2 and in the formation of Tp*M(S$_2$C$_2$R′$_2$)(SCNEt$_2$) complexes[26]). The melded-ligand complexes **A**/**B** are also precursors to bis(dithiolene)−Mo complexes analogous to **3**.[47] Mixed dithiocarbamate−thiocarboxamido complexes are relatively common,[48−55] but dithiolene−

(46) Miki, K.; Tanaka, N.; Kasai, N. *J. Organomet. Chem.* **1981**, *208*, 407−418.

(47) We have also observed that bis(dithiolene) complexes related to **3** are formed upon decomposition of complexes **A** and/or **B**. A preliminary crystal structure of [Et$_2$NCS$_2$C$_2$(R′)$_2$][Mo(S$_2$C$_2$R′$_2$)$_2$(S$_2$CNEt$_2$)] (R′ = CO$_2$Me) confirmed the presence of a trigonal prismatic anion. This observation provides an example of the generation of a dithiolene ligand via isolable melded-ligand complexes. Young, C. G.; Tiekink, E. R. T. Unpublished results.

(48) (a) Ricard, L.; Estienne, J.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1972**, 906−907. (b) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182−2186.

(49) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599−2605.

(50) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745−750.

(51) Brower, D. C.; Tonker, T. L.; Morrow, J. R.; Rivers, D. S.; Templeton, J. L. *Organometallics* **1986**, *5*, 1093−1097.

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thiocarboxamido complexes such as **2** have not been previously reported.

Microanalytical data confirmed that complexes **2** had the same formula as their counterparts in **1**. The IR spectra exhibited bands characteristic of dithiolene and dithiocarbamate ligands. Significantly, in addition to dithiocarbamate ν(CN) bands,[28] all the complexes exhibited strong absorptions at ca. 1590 cm^{-1}; these were assigned to the thiocarboxamido ν(CN) vibration, consistent with literature reports.[49−59]

The ^1H and ^{13}C NMR spectra of **2** were consistent with fluxional behavior at room temperature but rigid structures at temperatures below ca. 233 K. Variable-temperature ^1H NMR spectra of **2a** and **2b** suggest their fluxionality is due to site exchange involving the thiocarboxamido ligand. Low-temperature spectra were indicative of molecular C_s symmetry, implying a capped trigonal prismatic or pseudo-dodecahedral geometry in the ground state; a pentagonal bipyramidal geometry is unlikely as the thiocarboxamide would be required to span equatorial and axial sites under C_s symmetry. The observation of two $-OCH_3$ signals, as well as two $-CH_3$ signals each for the dithiocarbamate and thiocarboxamido ligands, is consistent with this proposal. gHMQC experiments on **2a** allowed confident assignment of the two high-field signals (δ_H 2.75 and 3.17) to the dithiocarbamate ligand and the low-field (δ_H 3.48 and 4.05) signals to the thiocarboxamido ligand.

The ^{13}C NMR spectra of **2a** and **2b** confirmed C_s molecular symmetry. Two $-CH_3$ resonances were observed for each of the dithiocarbamate and thiocarboxamido ligands, but only one OCH_3 signal was observed, even at 233 K. Signals in the range δ 146−152 were assigned to the dithiolene carbons, while those around δ 165 were assigned to the CO_2Me atoms. Resonances in the ranges δ 191−193 and δ 226−228 were assigned to the dithiocarbamate S_2CNR_2 and thiocarboxamido $SCNR_2$ carbon atoms, respectively. Related complexes generally exhibit resonances in the ranges δ 200−215 (S_2CNR_2) and δ 227−264 ($SCNR_2$).[28,49,50,52−54]

The ^1H NMR spectra of **2c** and **2d** were consistent with the presence of several interconvertible isomers. For example, the room-temperature spectrum of **2c** exhibited two $=CH$ resonances at δ 8.6 and 9.2 and four NMe_2 resonances in the region δ 2.8−4.2, as well as the expected phenyl resonances. At 193 K, four $=CH$ resonances, six thiocarboxamide resonances, and the two original dithiocarbamate resonances were observed. These observations are interpreted in terms of a mixture of isomers a and b (both of C_s symmetry) and enantiomeric c (C_1 symmetry) at low temperature (see Figure 6). The thiocarboxamido ligand of **2** may be considered

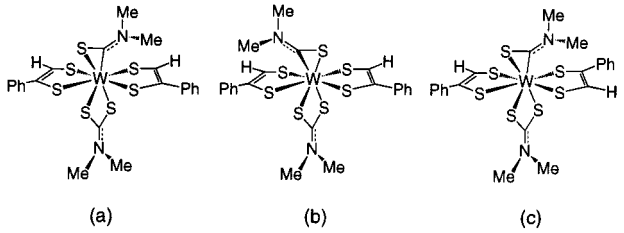

Figure 6. Possible capped trigonal prismatic or dodecahedral isomers of **2c**.

to occupy one or two coordination sites, leading to seven- or eight-coordinate descriptions, respectively. The ^1H NMR data are consistent with thiocarboxamido-capped trigonal prismatic or dodecahedral structures but eliminate a thiocarboxamido-capped octahedral structure. The thiocarboxamido methyl groups appear to be more sensitive to the arrangement of the dithiolene substituents than those of the dithiocarbamate ligand, giving resolved resonances for each isomer. Coincidental overlap of two $=CH$ resonances accounts for the observation of only four such resonances at low temperature. The ^{13}C NMR spectra of **2c** and **2d** revealed signals assignable to the dithiolene $=CH$ and $=CPh$ signals at δ 137−140 and 155−159, respectively. gHMQC again showed cross-peaks for the dithiolene carbon resonances and the proton signals at low field. The ^{13}C signals due to the κ^4 ligand CH and CPh atoms of **1c/d** were absent. The thiocarboxamido carbons resonate at δ 235 (R = Me) and 231 (R = Et).

Formation of Anionic Bis(dithiolene) Complexes. The green thiocarboxamido complexes **2** were unstable in methanolic solutions, being converted to orange, anionic complexes, $[W(S_2C_2R'_2)_2(S_2CNR_2)]^-$ (**3**), which may be isolated as tetraalkylammonium salts. Stirring **1** in acetonitrile also produces moderate yields of **3**. The conversion of **2→3** was quantitative, as assessed by changes to the UV−visible spectra of 1:1 CH_2Cl_2/MeOH solutions of **2** with time. In the specific case of the **2a→3a** conversion, decay of the band at 686 nm was accompanied by the growth of bands at 415 and 480 nm, with an isosbestic point at ca. 535 nm (Figure 5b). A possible mechanism involves nucleophilic attack of the thiocarboxamide by methanol to form $R_2NC(S)OR$,[60] which may transform to $R_2NC(S)Cl$[61] in chlorinated solvents. The organic byproduct(s) of the reaction have not been identified, but the white solids precipitated from synthetic reactions appear to be polymeric in nature.

In the IR spectra of the complexes, the thiocarboxamido ν(CN) bands of **2** were absent, but bands due to the dithiocarbamate and dithiolene ligands and countercation were observed. The ^1H NMR spectra of the various salts confirmed the presence of the countercation as well as a 1:2 ratio of dithiocarbamate and dithiolene ligands. The simple spectra observed were consistent with C_{2v} symmetry and the equivalence of

(52) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K. *J. Am. Chem. Soc.* **1986**, *108*, 310−311.
(53) Jeffery, J. C.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 567−572.
(54) Young, C. G.; Bruck, M. A.; Wexler, P. A.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1992**, *31*, 587−593.
(55) Gilletti, P. F.; Femec, D. A.; Keen, F. I.; Brown, T. M. *Inorg. Chem.* **1992**, *31*, 4008−4012.
(56) Treichel, P. M.; Dean, W. K. *J. Chem. Soc., Chem. Commun.* **1972**, 804−805.
(57) Desmond, T.; Lalor, F. J.; O'Sullivan, B.; Ferguson, G. *J. Organomet. Chem.* **1990**, *381*, C33−C37.
(58) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Butcher, R. J. *Organometallics* **1995**, *14*, 3370−3376.
(59) Ogric, C.; Lehotkay, T.; Wurst, K.; Jaitner, P.; Kreissel, F. R. *J. Organomet. Chem.* **1997**, *541*, 71−75.
(60) (a) Scully, F. E., Jr.; Ortega, T. *J. Org. Chem.* **1989**, *54*, 2978−2980. (b) Chen, L.; Thompson, T. R.; Hammer, R. P.; Barany, G. *J. Org. Chem.* **1996**, *61*, 6639−6645.
(61) (a) Goshorn, R. H.; Levis, W. W., Jr.; Jaul, E.; Ritter, E. J. *Organic Syntheses;* Wiley: New York, 1963; Collect. Vol. 4, pp 307−310. (b) Fieser, M.; Fieser, L. *Reagents for Organic Synthesis*; Wiley: New York, 1969; Vol. 2, p 173; Vol. 3, p 127; Vol. 5, p 202; Vol. 8, p 200. (c) Heckley, P. R.; Holah, D. G.; Brown, D. *Can. J. Chem.* **1971**, *49*, 1151−1160.

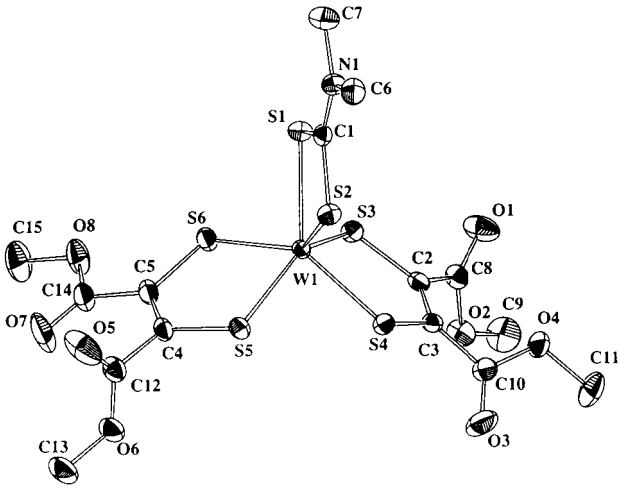

Figure 7. Molecular structure and atom-numbering scheme for the anion of NEt_4[**3a**].

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Anion of NEt_4[3a]

W(1)−S(1)	2.4475(15)	W(1)−S(2)	2.4626(15)
W(1)−S(3)	2.3616(14)	W(1)−S(4)	2.3369(14)
W(1)−S(5)	2.3642(13)	W(1)−S(6)	2.3407(14)
S(1)−C(1)	1.714(5)	S(2)−C(1)	1.716(5)
C(1)−N(1)	1.331(6)	S(3)−C(2)	1.745(5)
S(4)−C(3)	1.745(5)	C(2)−C(3)	1.348(7)
S(5)−C(4)	1.730(5)	S(6)−C(5)	1.755(5)
C(4)−C(5)	1.351(7)		
S(1)−W(1)−S(2)	69.86(5)	S(1)−W(1)−S(3)	84.46(5)
S(1)−W(1)−S(4)	131.93(5)	S(1)−W(1)−S(5)	130.72(5)
S(1)−W(1)−S(6)	85.94(5)	S(2)−W(1)−S(3)	131.61(5)
S(2)−W(1)−S(4)	85.68(5)	S(2)−W(1)−S(5)	83.45(5)
S(2)−W(1)−S(6)	131.61(5)	S(3)−W(1)−S(4)	82.11(5)
S(3)−W(1)−S(5)	140.59(5)	S(3)−W(1)−S(6)	84.07(5)
S(4)−W(1)−S(5)	83.85(5)	S(4)−W(1)−S(6)	137.59(5)
S(5)−W(1)−S(6)	81.95(5)	W(1)−S(1)−C(1)	90.28(17)
W(1)−S(2)−C(1)	89.74(17)	S(1)−C(1)−S(2)	110.1(3)
W(1)−S(3)−C(2)	108.62(16)	W(1)−S(4)−C(3)	109.53(17)
S(3)−C(2)−C(3)	120.1(4)	S(4)−C(3)−C(2)	119.6(4)
W(1)−S(5)−C(4)	108.88(18)	W(1)−S(6)−C(5)	109.41(18)
S(5)−C(4)−C(5)	120.6(4)	S(6)−C(5)−C(4)	119.1(4)

the two dithiocarbamate alkyl groups, and the four methylcarboxy groups. A trigonal prismatic structure may be inferred. The low solubility of these complexes prevented the collection of ^{13}C NMR data.

Crystal Structure of NEt_4[3a]. The crystal lattice of NEt_4[**3a**] is composed of discrete tetrahedral NEt_4^+ cations and trigonal prismatic **3a** anions; the structure of the anion is shown in Figure 7, and selected bond distances and angles are presented in Table 3. The trigonal faces, defined by atom sets {S(1),S(3),S(6)} and {S(2),S(4),S(5)}, are characterized by S···S distances in the range 3.141(2)−3.265(2) Å; the relative twist of the faces around the pseudo-3-fold axis is close to the ideal value of 0° for a trigonal prism.[62] Two of the lateral faces are shortened along one edge (S(1)···S(2) = 2.811(2) Å) due to the smaller normalized bite of the dithiocarbamate ligand (b = 1.145 Å) compared to the dithiolene ligands (b_{av} = 1.312 Å, S(3/5)···S(4/6) = 3.086(2) Å). The dithiocarbamate framework is planar (max. deviation 0.024(3) Å for C(7)), as are the dithiolene WS_2C_2 units (max. deviations 0.006(3) Å for C(2) and 0.024(2) Å for S(5)). The WS_2C_4 fragment containing S(3) is also planar (max. deviation 0.025(3) Å for C(10)), but the other deviates somewhat from planarity (max. deviation 0.106(3) Å for C(12)) due to intermolecular interactions. Atom W(1) lies only 0.057(4) Å out of the mean plane of the dithiocarbamate ligand. The metrical parameters of the ligands are consistent with related structures in the literature.[63] In particular, the core structure of **3a** is virtually superimposable on that of the anion of $NBu_4[Mo(mnt)_2(S_2CNMe_2)]$.[64]

(62) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1−65.

Summary

Novel κ^4 ligand complexes, **1**, were synthesized by reaction of $WS(S_2)(S_2CNR_2)_2$ with DMAC or phenylacetylene. The complexes have been fully characterized by microanalytical and spectroscopic techniques. The presence of the unique κ^4 ligand was confirmed by the X-ray crystal structure of **1a**·0.5H_2O. These complexes rearrange photochemically to form bis(dithiolene)thiocarboxamido complexes, **2**, which in turn convert to anionic, bis(dithiolene) complexes, **3**. The crystal structure of NEt_4[**3a**] revealed the presence of a trigonal prismatic complex anion.

The chemistry reported herein highlights the facile reactivity of sulfur-rich metal−dithiocarbamate complexes toward alkynes. Further, it highlights the propensity of alkynes to sequester available sulfur atoms for the construction of dithiolene ligands and provides new mechanistic insights into this process. These insights are afforded by an ability to isolate and fully characterize the relatively stable tungsten complexes in the sequence, $WS(S_2)(S_2CNR_2)_2$→**1**→**2**→**3**. Photochemical decomposition of the κ^4 ligands represents a novel and potentially useful synthetic strategy for dithiolene complexes.

Experimental Section

Materials and Methods. Samples of $WS(S_2)(S_2CNR_2)_2$,[21] $(NH_4)_2[WO_2S_2]$,[65] and $(NH_4)_2[WOS_3]$[65] were prepared by literature methods. The alkynes and thiuram disulfides were obtained from Aldrich Chemical Co. and used as received. Infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer as pressed KBr disks. ^1H and ^{13}C NMR spectra were obtained using Varian FT Unity300, Unity+400, or INOVA400WB spectrometers and were referenced to internal $CHCl_3$ (δ_H 7.26, δ_C 77.0). gHMQC and gHMBC experiments were performed using a slight modification[34] of standard pulse sequences.[31−33] UV−visible spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses. 1a. A solution of green $WS(S_2)(S_2CNMe_2)_2$ (1.816 g, 3.49 mmol) in dichloromethane (50 mL) was treated with DMAC (1 mL, 8.13 mmol), whereupon an immediate color

(63) Structurally characterized tungsten tris(dithiolene) complexes (and θ angles) include $(AsPh_4)_2[W(mnt)_3]$ (28°): Brown, G. F.; Stiefel, E. I. *Inorg. Chem.* **1973**, *12*, 2140−2047. $(PPh_4)_2[W(S_2C_2S_2CO)_3]$ (ca. 28°): Yang, X.; Freeman, G. K. W.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 3034−3038. $NMe_4[W(S_2C_6H_4)_3]$: Knock, F.; Sellmann, D.; Kern, W. *Z. Kristallogr.* **1992**, *202*, 326. $PHMe_2Ph[W(S_2C_6H_4)_3]$ (33°): Burrow, T. E.; Morris, R. H.; Hills, A.; Hughs, D. L.; Richards, R. L. *Acta Crystallogr., Sect. C* **1993**, *49*, 1591−1594. $(NBu_4)_2[W(S_5C_3)_3]$ (16°) and $FeCp^*_2[W(S_5C_3)_3]$ (0°): Matsubayashi, G.; Douki, K.; Tamura, H.; Nakano, M.; Mori, W. *Inorg. Chem.* **1993**, *32*, 5990−5996. $(NEt_3Bz)[W(S_2C_2Ph_2)_3]$·0.5MeCN and $W(S_2C_2Ph_2)_3$ (0°): Goddard, C. A.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5389−5398. $(NEt_4)_2[W(S_2C_6H_4)_3]$ (3.5°): Reference 15c.

(64) Bosman, W. P.; Nieuwpoort, A. *Inorg. Chem.* **1976**, *15*, 775−780.

(65) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205−210.

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change to purple was observed. After stirring for 4 h, the volume of the solution was reduced to 10 mL, and crystals of the purple product were precipitated by addition of methanol (50 mL). Protection from light prevents formation of trace **2a**. Yield: 1.918 g, 68%. Anal. Calcd for $C_{18}H_{24}N_2O_8S_7W$: C, 26.86; H, 3.01; N, 3.48; S, 27.89. Found: C, 26.78; H, 3.05; N, 3.43; S, 27.72. IR (KBr): 2950 m; ν(C═O) 1731 vs, 1708 vs; ν(CN) 1539 s, 1510 m; 1430 m; 1399 s; 1295 m; ν(C−O) 1241 vs br; 1194 s; 1167 s; ν(CS) 1097 m; 1060 m; 1014 m; 993 m; 915 w; 782 m; 669 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.02, 3.19, 3.45, 3.53 (s, 3H, 4 CH_3); 3.47, 3.88, 3.90, 4.01 (s, 3H, 4 OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 39.1, 39.2, 45.7, 48.7 (4 *C*H_3); 53.0, 53.1, 53.4 (4 O*C*H_3); 82.9 ($^1J_{CW}$ 10 Hz), 98.8 ($^1J_{CW}$ 7 Hz) (κ^4 ligand C═C); 148.6, 156.5 (dithiolene C═C); 164.6, 166.2, 168.4, 171.2 (4 *C*O_2Me); 200.0 (S_2*C*NMe_2); 213.5 (κ^4 ligand S_2*C*NMe_2). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 415 sh (2330), 509 (5830), 605 sh (1460).

1b. A procedure analogous to that employed in the synthesis of **1a** was employed for the synthesis of **1b**. Yield: 0.902 g, 61%. Anal. Calcd for $C_{22}H_{32}N_2O_8S_7W{\cdot}0.5CH_2Cl_2$: C, 29.91; H, 3.68; N, 3.10; S, 24.84; Cl, 3.92. Found: C, 29.98; H, 3.85; N, 3.12; S, 25.57; Cl, 3.74. IR (KBr): 2956 w; ν(C═O) 1727, 1714 vs; ν(CN) 1518 s; 1460 m; 1437 m; 1383 w; 1352 w; 1280 m; ν(C−O) 1238 vs; 1203 m; 1168 m; ν(CS) 1063 m; 1035 w; 996 w; 915 w; 900 w; 778 w; 564 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.09, 1.23, 1.27, 1.38 (t, 3H, ^3J 7.2 Hz, 4 CH_2CH_3); 3.26−4.08 (m, 4 CH_2); 3.45, 3.87, 3.89, 4.00 (s, 4 OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 11.9, 12.0, 12.1, 12.6 (4 CH_2*C*H_3); 44.3, 44.3, 51.1, 52.6 (4 *C*H_2); 52.9, 53.0, 53.3, 54.7 (4 O*C*H_3); 81.6 ($^1J_{CW}$ 7 Hz), 98.8 ($^1J_{CW}$ 5 Hz) (κ^4 ligand C═C); 148.4, 156.7 (dithiolene C═C); 164.8, 166.4, 168.6, 171.4 (4 *C*O_2Me); 199.1 (S_2*C*NEt_2); 211.8 (κ^4 ligand S_2*C*NEt_2). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 410 sh (3290), 510 (6840), 615 sh (1690).

1c. A mixture of $WS(S_2)(S_2CNMe_2)_2$ (0.828 g, 1.59 mmol) and phenylacetylene (0.45 mL, 4.10 mmol) in 1,2-dichloroethane (60 mL) was refluxed for 1.5 h in air to yield purple, green (2 of), and orange products, which were separated (with some difficulty) by column chromatography on silica gel using 4:1 CH_2Cl_2/pentanes as eluent. Yield: 0.374 g, 33%. The yield of byproduct **2c** was typically 0.329 g, 29%. Anal. Calcd for $C_{22}H_{24}N_2S_7W$: C, 36.46; H, 3.34; N, 3.86, S 30.71. Found: C, 36.73; H, 3.31; N, 3.80; S, 30.83. IR (KBr): 3049 w; 3027 w; 2927 w; 2860 w; ν(C═C) 1592 m; ν(CN) 1523 vs br; 1476 s; 1441 m; 1395 vs; 1255 m; 1226 m; 1152 s br; 1073 w; 1054 w; 1028 w; 991 m; 970 m; 941 w; 910 w; 881 w; 852 w; 792 w; ν(Ph) 754 s; 733 m; ν(Ph) 696 s; 673 w; 614 w; 592 m; 505 w; 457 w; 442 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz), 2:1 mixture of isomers: δ 2.97, 3.24, 3.44, 3.49 (s, 3H, 4 CH_3); 5.57 (major), 5.61 (minor) (s, total 1H, κ^4 ligand C*H*); 7.21−7.88 (m, 10H, Ph); 8.90 (minor, $^2J_{HW}$ 10.8 Hz), 9.10 (major, $^2J_{HW}$ 11.6 Hz) (s, total 1H, dithiolene C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz), 2:1 mixture of isomers: δ 39.2, 39.3, 45.3, 48.8 (*C*H_3); 68.7 (minor), 68.9 (major) (κ^4 ligand *C*H); 101.0 (minor), 101.1 (major) (κ^4 ligand *C*Ph); 126.6−144.0 (Ph); 139.6 (minor), 144.0 (major) (dithiolene *C*H); 157.8 (major), 162.9 (minor) (dithiolene *C*Ph); 202.4 (S_2*C*NMe_2); 218.4 (κ^4 ligand S_2*C*NMe_2). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 389 sh (6150), 528 (6390), 660 (1440).

1d. A mixture of $WS(S_2)(S_2CNEt_2)_2$ (0.960 g, 1.67 mmol) and phenylacetylene (0.8 mL, 7.28 mmol) in toluene (30 mL) was heated in air at 85 °C for 18 h. Workup was carried out as for **1c** except 3:2 CH_2Cl_2/pentanes was used as eluent. Yield: 0.125 g, 10%. Green **2d** was also obtained from the reaction. Yield: 0.184 g, 14%. Anal. Calcd for $C_{26}H_{32}N_2S_7W$: C, 39.99; H, 4.13; N, 3.59; S, 28.74. Found: C, 40.16; H, 4.13; N, 3.39; S, 28.48. IR (KBr): 3051 w; 2974 m; 2932 m; 2871 w; ν(C═C) 1592 m; 1564 m br; ν(CN) 1504 vs br; 1474 s; 1457 s; 1438 vs; 1380 m; 1355 m; 1275 s; 1210 m; 1186 w; 1149 m; 1075 m; 1029 m; 1003 m; 978 w; 913 w; 848 w; 807 m br; ν(Ph) 754 s; ν(Ph) 693 m; 611 w; 588 m; 559 w; 448 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz), 2:1 mixture of isomers: δ 0.97−1.34 (m, 12H, 4 CH_3); 3.21−4.41 (m, 8H, 4 CH_2); 5.62 (major), 5.66 (minor) (s, total 1H, κ^4 ligand C*H*); 7.21−7.96 (m, 10H, Ph); 8.90 (minor, $^2J_{HW}$ 7.2 Hz), 9.09 (major, $^2J_{HW}$ 8.1 Hz) (s, total 1H, dithiolene C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz) 2:1 mixture of isomers: δ 11.9, 12.3, 12.4, 12.7 (*C*H_3); 44.4, 44.5, 50.7, 54.8 (*C*H_2); 68.4 (minor), 68.6 (major) (κ^4 ligand *C*H); 100.9 (minor), 101.1 (major) (κ^4 ligand *C*Ph); 126.7−139.4 (Ph); 139.8 (major), 143.9 (minor) (dithiolene *C*H); 157.3 (major), 162.7 (minor) (dithiolene *C*Ph); 201.7 (S_2*C*NEt_2); 216.7 (κ^4 ligand S_2*C*NEt_2).

2a. Purple **1a** (1.000 g, 1.24 mmol) was dissolved in dichloromethane (100 mL) in air and irradiated by sunlight for 2−3 h. The volume of the solution was then reduced to 10 mL (rotary evaporation), and methanol (50 mL) was added to precipitate green crystals. These were isolated by filtration, washed with methanol, and vacuum-dried. Yield: 0.791 g, 79%. Anal. Calcd for $C_{18}H_{24}N_2O_8S_7W$: C, 26.87; H, 3.01; N, 3.48; S, 27.89. Found: C, 27.00; H, 3.03; N, 3.43; S, 27.66. IR (KBr): 2998 w; 2951 m; ν(C═O) 1720 vs br; ν(CN) 1594 s, 1544 s; 1514 m; 1430 s; 1403 s; ν(C−O) 1244 vs br; ν(CS) 1091 m; 1023 m; 927 m; 914 m; 766 w; 692 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 233 K): δ 2.75, 3.17 (s, 3H, 2 CH_3 of S_2CNMe_2); 3.48 (s, 3H, CH_3 of $SCNMe_2$); 3.86, 3.93 (s, 6H, 4 OCH_3); 4.05 (s, 3H, CH_3 of $SCNMe_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 38.9, 39.2 (2 *C*H_3 of S_2CNMe_2); 43.7, 55.2 (2 *C*H_3 of $SCNMe_2$); 53.1 (4 O*C*H_3); 146.3, 151.3 (2 C═C); 165.5 (4 *C*O_2Me); 192.8 (S_2*C*NMe_2); 227.9 ($SCNMe_2$). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 407 (4690), 583 sh (3780), 680 (9340).

2b. In a procedure similar to that used for **2a**, a dichloromethane (50 mL) solution of **1b** (0.506 g, 0.590 mmol) was stirred in sunlight for 2 h. After workup as above, the green crystals were obtained by cooling the CH_2Cl_2/MeOH mixture to −4 °C. Yield: 0.395 g, 78%. Anal. Calcd for $C_{22}H_{32}N_2O_8S_7W$: C, 30.70; H, 3.75; N, 3.25; S, 26.07. Found: C, 30.70; H, 3.70; N, 3.26; S, 26.10. IR (KBr): 2951 m; ν(C═O) 1731 vs, 1720 vs, 1708 vs; ν(CN) 1594 s, 1544 s, 1514 m; 1431 s; 1403 s; ν(C−O) 1243 vs br; ν(CS) 1091 m; 1023 m; 927 m; 769 m; 693 m br cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.00, 1.10, 1.29, 1.70 (t, 3H, ^3J 7.2 Hz, 4 CH_3); 3.20, 3.60, 3.63 (q, 2H, ^3J 7.2 Hz, 3 CH_2); 3.90 (s br, 12H, 4 OCH_3); 4.36 (q, 2H, ^3J 7.2 Hz, CH_2). ^{1}H NMR (CD_2Cl_2, 400 MHz, 193 K): δ 0.97, 1.06, 1.27, 1.70 (t, 3H, ^3J 7.2 Hz, 4 CH_3); 3.20, 3.62, 3.63 (q, 2H, ^3J 7.2 Hz, 3 CH_2); 3.81, 3.90 (s, 6H, 4 OCH_3); 4.34 (q, 2H, ^3J 7.2 Hz, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.52 MHz, 233 K): δ 11.0, 11.8, 12.6, 15.3 (4 CH_2*C*H_3); 43.6, 44.1, 49.6, 60.0 (4 *C*H_2); 53.3 (4 O*C*H_3); 147.2, 149.4 (2 C═C); 165.1, 165.5 (4 *C*O_2Me); 190.8 (S_2*C*NEt_2); 226.4 ($SCNEt_2$). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 415 (5030), 585 sh (4120), 685 (9010).

2c. This complex was isolated as a byproduct in the synthesis of **1c** but can also be prepared by irradiation of **1c**. Anal. Calcd for $C_{22}H_{24}N_2S_7W$: C, 36.46; H, 3.34; N, 3.86; S, 30.96. Found: C, 36.19; H, 3.34; N, 3.77; S, 31.15. IR (KBr): 3050 w; 3019 w; 2923 w; 2859 w; ν(C═C) 1643 w; ν(CN) 1576 s br, 1530 s br; 1472 vs; 1439 s; 1396 vs; 1254 m; 1217 m; 1153 s br; 1073 w; 1030 m; 1002 w; 927 m; 846 m; 824 m; 797 m; 752 vs; 693 s; 611 m; 587 w; 556 m; 488 w; 447 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.77, 3.18, 3.44, 4.09 (s, 4 CH_3); 7.24−7.40 (m, 6H, Ph); 7.79, 7.97 (d, 4H, Ph); 8.61 (s, ═C*H*); 9.19 (s, ═C*H*). ^{1}H NMR ($CDCl_3$, 400 MHz, 213 K), mixture of three isomers: δ 2.77, 3.18 (s, CH_3 of S_2CNMe_2); 3.44, 3.45, 3.47, 4.07, 4.09, 4.10 (s, CH_3 of $SCNMe_2$); 7.22−7.46 (m, Ph); 7.80, 7.99 (d, Ph, ^3J 7.6 Hz); 8.63, 8.65, 9.19, 9.22 (s, ═C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.4 MHz): δ 38.8, 39.1 (2 *C*H_3 of S_2CNMe_2); 43.5, 54.4 (2 *C*H_3 of $SCNMe_2$); 127.3, 127.6, 128.0, 128.2, 129.2, 129.7 (Ph); 136.5, 140.4 (2 ═*C*H); 155.0, 159.4 (2 ═*C*Ph); 194.0 (S_2CNMe_2); 234.5 ($SCNMe_2$). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 400 (4970), 607 (3330), 724 (11150).

2d. This complex was prepared as a byproduct in the synthesis of **1d** or upon irradiation of **1d**. Anal. Calcd for

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$C_{26}H_{32}N_2S_7W$: C, 39.99; H, 4.13; N, 3.59; S, 28.74. Found: C, 40.82; H, 4.19; N, 3.36. IR (KBr): 3052 w; 3018 w; 2973 m; 2931 w; 2869 w; ν(C═C) 1653 w br; ν(CN) 1591 m, 1562 m br, 1504 vs br; 1473 s; 1458 s; 1437 vs; 1380 m; 1353 m; 1275 s br; 1211 m; 1186 m; 1149 m; 1091 m sh; 1074 m; 1029 m; 1001 m br; 937 w; 896 w; 848 m; 805 m br; 752 s; 693 m; 610 m; 585 w; 555 w; 466 w br cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 233 K): δ 0.94, 1.09, 1.25, 1.77 (t, ^3J 7.2−7.5 Hz, 4 CH_3); 3.07−3.61, 4.34−4.41 (m, 4 CH_2); 7.23−7.46 (m, 6H of Ph); 7.77, 8.00 (d, ^3J 7.2 Hz, 4H of Ph); 8.65, 8.68, 9.15 (s, ═CH). ^{13}C NMR ($CDCl_3$, 100.52 MHz): δ 11.4, 12.1, 12.8, 15.2 (4 CH_3); 43.6, 44.0, 49.6, 59.0 (4 CH_2); 128.0, 128.2 (Ph); 136.5, 139.5 (2 ═CH); 157.5 (═CPh); 201.0 (S_2CNEt_2); 231.0 ($SCNEt_2$). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 404 (5050), 615 (3650), 726 (9050).

NMe$_4$[3a], Method A. A dichloromethane solution (15 mL) of $WS(S_2)(S_2CNMe_2)_2$ (0.604 g, 1.16 mmol) and DMAC (0.2 mL, 1.63 mmol) was stirred for 3 h to yield purple **1a**. The solvent was removed by rotary evaporation, and the residue was recrystallized from dichloromethane/methanol. The solid obtained was immediately dissolved in dichloromethane (50 mL), and the solution was stirred under direct sunlight for 2.5 h. The resulting green solution was reduced to dryness by rotary evaporation and the residue dissolved in 1:1 dichloromethane/methanol (v/v, 50 mL) and stirred overnight. The solvent was removed by rotary evaporation and the residue dissolved in 1,2-dichloroethane. Treatment with methanol precipitated white solids, which were filtered off. A solution of NMe_4Cl (1.0 g, 9.12 mmol) in ethanol (30 mL) was then added to the filtrate to yield red microcrystals. Recrystallization from dichloromethane/methanol yielded 0.120 g of the product (13% yield based on $WS(S_2)(S_2CNMe_2)_2$).

Method B. In a round-bottom flask, green **2a** (0.200 g, 0.249 mmol) was stirred in 1:1 dichloromethane/methanol (v/v, 50 mL) overnight at room temperature. The orange solution obtained was reduced to dryness by rotary evaporation and the residue then treated with dichloromethane (2 mL) and ethanol (15 mL) to precipitate the white organic byproduct(s). The mixture was filtered into an ethanolic solution (30 mL) of NMe_4Cl (1.0 g, 9.12 mmol) to precipitate orange microcrystals. Yield: 0.050 g, 26%. Anal. Calcd for $C_{19}H_{30}N_2O_8S_6W$: C, 28.86; H, 3.82; N, 3.54; S, 24.33. Found: C, 28.90; H, 3.77; N, 3.53; S, 24.03. IR (KBr): 3018 w; 2950 m; ν(C═O) 1710 vs; ν(CN) 1533 s; 1485 m; 1435 m; 1403 m; ν(C−O) 1232 vs; 1158 m; ν(CS) 1080 m; 1013 m; 948 m; 892 w; 769 w; 688 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.48 (s, 4 CH_3 of NMe_4^+), 3.10 (s, 2 CH_3 of S_2CNMe_2), 3.84 (s, 4 OCH_3).

NEt$_4$[3a]. A 1:1 dichloromethane/methanol (v/v, 50 mL) solution of **2a** (0.509 g, 0.633 mmol) was refluxed in air for 4 h. The volume of the solvent was reduced to almost dryness to yield an oily residue, which was taken up in a minimum amount of dichloromethane. This was added to a solution of NEt_4Cl (1.6 g, 8.71 mmol) in ethanol (20 mL) to precipitate orange needles, which were filtered, washed with ethanol, and dried in vacuo. Yield: 0.405 g, 76%. IR (KBr): 2991 w; 2947 w; ν(C═O) 1713 s; ν(CN) 1544 w; 1523 m; 1482 w; 1435 m; 1400 m; ν(C−O) 1238 vs; 1172 w; 1074 w; 1020 w; 895 w; 791 w; 693 cm^{-1}. Electronic spectrum (CH_2Cl_2) λ nm (ϵ M^{-1} cm^{-1}): 413 (7500), 480 (4300), 616 (370).

N^{n}Bu$_4$[3a]. A suspension of $WS(S_2)(S_2CNMe_2)_2$ (0.293 g, 0.563 mmol) in dichloromethane (50 mL) was treated with DMAC (0.1 mL, 0.813 mmol) and stirred for 3 h until all the reactant had been consumed to form purple **1a**. The solution was reduced to dryness, and the residue was redissolved in acetonitrile, which was then stirred in air. When the purple complex was completely consumed, the mixture was filtered and the filtrate was evaporated to dryness. The residue was then taken up in dichloromethane and added into an ethanolic solution of $N^nBu_4Cl\cdot H_2O$ (0.697 g, 2.51 mmol). The solution was allowed to stir for 30 min and then stripped down to dryness and the residue recrystallized from CH_2Cl_2/EtOH. Yield: 0.198 g, 37%. IR (KBr): 2961 m; 2876 w; ν(C═O) 1707 s br; ν(CN) 1538 m sh, 1522 m; 1479 w; 1460 w; 1429 m; 1401 m; 1383 w; ν(C−O) 1233 vs br; 1156 w; 1079 w; 1017 w; 977 w; 896 w; 814 m; 772 w; 755 w; 696 w; 587 w; 445 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.90 (t, ^3J 7.5 Hz, 4 CH_3 of NBu_4^+), 1.26 (s br, 8 CH_2 of NBu_4^+), 2.54 (s br, 4 CH_2 of NBu_4^+), 3.11 (s br, 2 CH_3 of S_2CNMe_2), 3.81 (s, 4 OCH_3).

Table 4. Crystallographic Data

	1a·0.5H_2O	NEt_4[**3a**]
formula	$C_{18}H_{25}N_2O_{8.5}S_7W$	$C_{23}H_{38}N_2O_8S_6W$
fw	813.67	846.76
cryst syst	monoclinic	triclinic
space group	$P2_1$	$P\bar{1}$
a (Å)	11.873(4)	9.278(3)
b (Å)	12.229(9)	13.794(4)
c (Å)	20.913(3)	14.174(2)
α (deg)	90	71.82(3)
β (deg)	93.68(2)	76.68(2)
γ (deg)	90	78.16(3)
V (Å^3)	3030(1)	1659.6(8)
Z	4	2
ρ_{calc} (g/cm^3)	1.783	1.695
T (K)	293(1)	293(2)
diffractometer	Rigaku AFC6R	Enraf Nonius
radiation, λ	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
μ (cm^{-1})	43.42	39.02
R^a	0.042	0.031
R_w/wR_2	0.056^b	0.080^c

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum(w|F_o|^2)]^{1/2}$. ^{c} $wR_2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum(w|F_o^2|^2)]^{1/2}$.

NMe$_4$[3b]. A solution of **2b** (0.383 g, 0.445 mmol) in 1:1 dichloromethane/methanol (v/v, 30 mL) was refluxed overnight to obtain an orange solution. The solvent was removed by rotary evaporation, and the residue was dissolved in a minimum of dichloromethane and treated with ethanol (30 mL). The resulting mixture was filtered into an ethanolic solution (30 mL) of NMe_4Cl (1.0 g, 9.12 mmol) to obtain orange crystals of the product. Yield: 0.095 g, 26%. IR (KBr): 3018 w; 2950 m; ν(C═O) 1721 s, 1708 s; ν(CN) 1524 s; 1485 m; 1437 m; 1382 w; 1359 w; ν(C−O) 1235 vs; 1150 w; ν(CS) 1082 m; 1015 m; 982 m; 948 m; 816 m; 776 w; 687 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (t, ^3J 7.2 Hz, 2 CH_3 of S_2CNEt_2), 2.72 (s br, 4 CH_3 of NMe_4^+), 3.50 (q, ^3J 7.2 Hz, 2 CH_2 of S_2CNEt_2), 3.84 (s, 4 OCH_3).

WO(S$_2$)(S$_2$CNEt$_2$)$_2$. (a) From (NH$_4$)$_2$[WOS$_3$]. Acetonitrile (40 mL) was added to a mixture of $(NH_4)_2[WOS_3]$ (1.10 g, 3.31 mmol) and $(S_2CNEt_2)_2$ (2.48 g, 8.36 mmol) in a Schlenk flask. The mixture was stirred for 1 h, and the resultant red-orange precipitate $[WO(S_2)(S_2CNEt_2)_2$ and $(S_2CNEt_2)_2]$ was isolated by filtration, washed with cold acetonitrile, and dried at the pump. Recrystallization from CH_2Cl_2/EtOH resulted in the isolation of pure dark maroon $WO(S_2)(S_2CNEt_2)_2$. Yield: 1.311 g, 71%.

(b) From (NH$_4$)$_2$[WO$_2$S$_2$]. Acetonitrile (40 mL) was added to a mixture of $(NH_4)_2[WO_2S_2]$ (1.00 g, 3.16 mmol) and $(S_2CNEt_2)_2$ (2.36 g, 7.96 mmol), and the mixture was refluxed for 3−4 h to yield red microcrystals of $WO(S_2)(S_2CNEt_2)_2$. The product was filtered in air, washed with cold acetonitrile, and dried in vacuo. Yield: 1.00 g, 57%. Spectroscopic data for the products from both methods were identical to those reported in the literature.[22]

X-ray Crystallography. Crystals of **1a**·0.5H_2O were obtained by slow diffusion of hexane into a dichloromethane solution of the complex under light-free, anaerobic conditions. Crystals of NEt_4[**3a**] were obtained by slow diffusion of methanol into a dichloromethane solution of the complex. Crystallographic data are summarized in Table 4.

Intensity data for **1a**·0.5H_2O were collected at room temperature on a Rigaku AFC6R diffractometer fitted with Mo Kα radiation. The $\omega-2\theta$ scan technique was used to measure 7674 data such that θ_{max} was 27.5°. Corrections were applied

for Lorentz and polarization effects,[66] and an empirical absorption correction was applied.[67] The structure was solved by direct methods[68] and refined by a full-matrix least-squares procedure based on F[66] for 5816 data with $I > 3.0\sigma(I)$. Non-H atoms were refined anisotropically except for the partially (50%) occupied water molecules of crystallization; H atoms were included in their calculated positions. Significant thermal motion was noted in some of the atomic positions, but multiple sites were not detected. The absolute structure was determined by inverting the structure and comparing the refinements, and an extinction correction was applied. The largest residual (1.30 e Å^{-3}) was located in the vicinity of W(2). The data were modeled so that two independent molecules comprise the asymmetric unit in the non-centrosymmetric space group $P2_1$. As mentioned in the text, these molecules are pseudo-enantiomeric, and thus, a shift in the origin potentially leads to a centrosymmetric space group (with one independent molecule). The presence of a significant number of reflections that should be absent if a glide plane was present (e.g., 192 for $P2_1/c$) precludes space group No. 14. Support for the non-centrosymmetric choice is found in the distribution of E-statistics. Further, no chemically sensible solution to the structure could be found in $P2_1/m$. The diagram (Figure 3) showing the atomic numbering scheme was drawn with ORTEP[69] at the 40% probability level.

Reflection data for NEt_4[**3a**] were collected at 293(2) K on an Enraf Nonius CAD4f diffractometer using the $\omega-2\theta$ scan method and Mo Kα radiation. Unit cell parameters were determined from 25 reflections, with intensity statistics consistent with the triclinic space group $P\bar{1}$. A total of 6206 reflections were measured, of which 5814 were unique (R_{int} 0.016). Absorption corrections were evaluated by analytical methods ($\mu_{Mo\ K\alpha}$ 3.90 mm^{-1}) and applied to the data, the maximum and minimum transmission factors being 0.5961 and 0.4061, respectively. The structure was solved by direct methods (SHELXS-86[70]) and refined using full-matrix least-squares on F^2 (SHELXL-97[71]). The NEt_4^+ cations were found to be disordered at the methylene carbon positions, the occupancy of the disordered atoms being split equally over two positions (the eight methylene sites occupying the vertexes of a regular cube). Hydrogen atoms were included in idealized positions with isotropic displacement factors on all unsaturated carbons with the exception of those on the NEt_4^+ cation. Final refinement was carried out using a weighting scheme of the type $[\sigma^2(F_o^2) + (0.0514P)^2 + 0.6500P]^{-1}$, where $P = (F_o^2+2F_c^2)/3$. At convergence R [$I \geq 2\sigma(I)$] = 0.031 and wR_2 (all data) = 0.080. The largest residual peak in the final difference Fourier map was 1.45 e Å^{-3}, 0.99 Å from W(1). The atomic scattering factors were those incoporated in the SHELXL-97 program.[71] Calculations were carried out on a Vaxstation 4000 VLC computer system. Figure 7 was generated using the program ZORTEP.[72]

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(66) *teXsan: Structure Analysis Software;* Molecular Structure Corp.: The Woodlands, TX, 1992.
(67) Walker, N.; Stuart, D. *Acta Crystallogr. Sect. A* **1983**, *39*, 158.
(68) Sheldrick, G. M. *SHELX86, Program for the Automatic Solution of Crystal Structure;* University of Göttingen: Germany, 1986.
(69) Johnson, C. K. *ORTEP.* Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
(70) Sheldrick, G. M. In *SHELXS-86*, in *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189.
(71) Sheldrick, G. M. *SHELXL-97 Program for Crystal Structure Refinement*; University of Gottingen: Germany, 1997.
(72) Zsolnsai, L. *ZORTEP, An Interactive ORTEP Program*; University of Heidelberg: Germany, 1994.