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Formation of Mono(dithiolene)–Thiocarboxamido Complexes in Reactions of Thio(dithiocarbamato)–Mo/W Complexes and Dimethyl Acetylenedicarboxylate

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Reactions of Tp*MS(S_2CNEt_2) with dimethyl acetylenedicarboxylate in dichloromethane produce olive green/black Tp*M$\{S_2C_2(CO_2Me)_2\}$($SCNEt_2$-$\kappa^2 S,C$) (M = Mo (**1**), W (**2**); Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate). The seven-coordinate complexes exhibit pseudo-octahedral (**1**) and distorted pentagonal bipyramidal (**2**) coordination spheres comprised of tridentate *fac*-Tp*, bidentate dithiolene, and thiocarboxamido-$\kappa^2 S,C$ ligands. In the solid state, molecules of **1** exhibit pseudo-C_s symmetry, with the thiocarboxamide NEt_2 group in a cleft in the Tp* ligand. Molecules of **2** have C_1 symmetry in the solid state; here, the thiocarboxamide unit is orientated along one of the W–S(dithiolene) bonds with its NEt_2 group projecting away from the Tp* ligand. Both complexes possess effective C_s symmetry in solution. Reaction of Tp*MoI$(CO)_3$ with AgS_2CNEt_2 affords olive green Tp*Mo(S_2CNEt_2)$(CO)_2$ (**3**), which reacts with propylene sulfide in a new synthesis for Tp*MoS(S_2CNEt_2), the starting material for **1**. Complex **3** exhibits a distorted pentagonal bipyramidal structure, the axial sites being defined by a Tp* nitrogen atom and a carbonyl ligand, the pentagonal plane by the remaining nitrogen and carbonyl donors and the two sulfur atoms of the bidentate dithiocarbamate ligand.

Introduction

The unique electronic, spectral, magnetic, and redox properties of metallodithiolenes make them attractive candidates for a myriad of technological applications including their use in inks and dyes, optical, conducting, superconducting, and magnetic molecular materials, initiators for photooxidation reactions, antifouling agents, and catalysts.[1,2] The potential applications of dithiolene complexes even extend to the electrochemical separation and purification of olefins from refinery feedstocks.[3] Nature also exploits metallodithiolene centers in the active sites of pterin-containing Mo[4−7] and W[6−9] enzymes. Many of these enzymes possess bis(dithiolene) active sites, a fact that has stimulated much recent progress in the synthesis and study of complexes of this type.[10−13] Tris(dithiolene) complexes are also well represented in the literature, and Mo and W complexes have

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been recently reviewed.[12,13] Significantly fewer mono(dithiolene) complexes are known despite the presence of mono(dithiolene)−Mo enzyme centers in, for example, sulfite oxidase and the molybdenum hydroxylases.[4−7]

For many years, mono(dithiolene)−Mo complexes were restricted to oxo-Mo(IV) complexes of the type MoO(mnt)L (mnt = maleonitriledithiolate, L = amine or phosphine),[14] a class recently extended by Sugimoto et al.[15] Various hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) complexes, including Tp*MX(dithiolene) (M = Mo, X = NCS;[16] M = W, X = OPh[17,18]) and pseudo-dithiolene complexes such as Tp*MoE(bdt) (E = O,[10] S;[20] bdt = benzene-1,2-dithiolate) have also been prepared and studied by Enemark, Young, and others. Related cyclopentadienyl species, such as $PPh_4[Cp^*MoS(S_2C_2Ph_2)]$,[21] $PPh_4[Cp^*WS(S_2C_2PhR)]$ (R = H, Ph),[22] $Cp_2Mo(dddt)$ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate),[23] and $Cp_2Mo\{S_2C_2(2\text{-quin})(R)\}$ (quin = 2-quinoxalinyl, R = H, C(O)Me, etc.[24−26]), are also known. More recently, Holm and co-workers have expanded the number of known oxo-Mo mono(dithiolene) complexes, with the synthesis and characterization of square pyramidal complexes such as $[MoO_2(SC_6H_2{}^iPr_3\text{-}2,4,6)(bdt)]^-$, $[MoO(SAd)_2(S_2C_2Me_2)]^-$, $[MoO(SR)_2(bdt)]^-$ (R = 2-adamantyl (Ad), $C_6H_2{}^iPr_3$-2,4,6), and $[MoOCl(SC_6H_2{}^iPr_3\text{-}2,4,6)(bdt)]^-$.[27] Many of these complexes are excellent models for various molybdenum enzymes.

Broadly speaking, there are two principal synthetic strategies for the incorporation of dithiolene ligands into metal complexes: (i) reaction of a metal halide with a free or protected ene-dithiolate moiety, and (ii) reactions of various metal−sulfur complexes with alkynes.[28] Classic examples of the latter strategy involve reactions of metal di-, tetra-, and penta-sulfido complexes or bis- and tris(thio) species with alkynes.[28] The thermodynamic stability of bis- and tris(dithiolene) complexes and/or polynuclear species favors their formation. Mono(dithiolene) complexes may be synthesized by both strategies, but Mo and W complexes are accessible only when bulky co-ligands, for example, cyclopentadienyl or trispyrazolylborate ligands, are employed (vide supra).

Recently, there has been increasing interest in the intermediacy of “melded ligands” in the generation of dithiolene complexes from reactions between metal−sulfur species and alkynes.[29−31] Indeed, dithiolene ligand formation has been tracked in the reactions of $WS(S_2)(S_2CNEt_2)_2$ with dimethyl acetylenedicarboxylate (DMAC) and PhCCH.[31] Proposed mechanisms for the initial reaction in the sequence invoke initial attack by the thio ligand on an electrophilic alkyne carbon, followed by attack of the incipient carbanion on sulfur-donor co-ligands; subsequent reactions lead to the formation of bis(dithiolene) complexes. To test the feasibility of this mechanistic proposal, we have investigated the reactions of thio(dithiocarbamate) complexes, $Tp^*MS(S_2CNEt_2)$ (M = Mo, W), with DMAC. The outcomes of these reactions, the formation of mono(dithiolene) complexes, $Tp^*M\{S_2C_2(CO_2Me)_2\}(SCNEt_2)$ (M = Mo (**1**), W (**2**)), are consistent with initial attack involving the thio ligand followed by subsequent cleavage and sequestration of sulfur from the dithiocarbamate co-ligand. The reactions described add to the synthetic armory for mono(dithiolene) complexes and provide information about the mechanism of formation of organometallic ligand coupled products in related systems. The synthesis and characterization of $Tp^*Mo(S_2CNEt_2)(CO)_2$ (**3**), a precursor en route to **1**, are also described.

Experimental Section

Materials and Methods. The complexes $Tp^*MS(S_2CNEt_2)$ (M = Mo,[32] W[33]) were prepared by literature methods or using the synthesis described below (for M = Mo). Dimethyl acetylenedicarboxylate was purchased from Aldrich Chemical Co. and was used as received; all other reagents were AR grade or above. Anaerobic reactions were performed using dried and deoxygenated solvents and Schlenk and glovebox techniques. Infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer. NMR spectra were obtained using Varian FT Unity300 and UnityPlus 400 spectrometers and were referenced to internal $CHCl_3$ (δ_H = 7.26) or $CDCl_3$ (δ_C 77.36) unless otherwise stated. UV−visible spectra were recorded on a Hitachi 150-20 double beam spectrophotometer. High-resolution mass spectra were recorded via a

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VG7070F instrument or a Bruker BioApex 47e STMS fitted with an Analytica electrospray source. Cyclic voltammograms were recorded via a Cypress Electrochemical System II with a 3 mm glassy carbon working electrode and platinum auxiliary and reference electrodes. Solutions of the complexes (5−10 mM) in 0.1 M $N^{n}Bu_4PF_6$/dichloromethane were employed, and scans were referenced to internal ferrocene. Potentials are reported relative to the saturated calomel electrode (SCE) ($E_{1/2}(Fc^+/Fc) = 0.460$ V vs SCE[34]). EPR spectra were recorded on a Bruker FT ECS-106 spectrometer using 1,1-diphenyl-2-picrylhydrazyl as reference. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

Syntheses. Complex 1. Under anaerobic conditions, DMAC (0.20 mL, 1.6 mmol) was injected into a solution of Tp*MoS(S_2CNEt_2) (0.753 g, 1.31 mmol) in dichloromethane (30 mL). The mixture was stirred for 18−24 h, and then the solvent was removed in vacuo. The residue was column chromatographed in air (silica gel, 1:10 CH_3CN:CH_2Cl_2) and the dark green fraction was collected. Green crystals were obtained by enriching a dichloromethane solution with methanol (khaki or red-brown crystals were produced upon rapid precipitation). The crystals were isolated by filtration and washed with methanol. Yield: 0.297 g, 32%.

Anal. Calcd for $C_{26}H_{38}BMoN_7O_4S_3$: C, 43.64; H, 5.35; N, 13.70; S, 13.44. Found: C, 43.40; H, 5.23; N, 13.53; S, 13.66. Infrared (KBr): 2946 m, ν(BH) 2554 w, ν(C═O) 1722 and 1699 s, ν(CN) of Tp* 1546 s, ν(CN) of $SCNEt_2$ 1497 m, 1443 s, 1416 s, 1360 m, ν(C−O−C) 1228 vs, 1066 m, 1024 m, 854 w, 812 w, 687 w, 642 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.11 (t, ^3J 7.2 Hz, 3H), 1.34 (t, ^3J 7.2 Hz, 3H) (2 CH_3 of $SCNEt_2$); 2.25 (s, 3H), 2.55 (s, 3H), 3.13 (s, 6H), 3.31 (s, 6H) (6 CH_3 of Tp*); 3.92 (s, 6H, 2 CO_2CH_3); 4.24 (q, ^3J 7.2 Hz, 2H), 5.04 (q, ^3J 7.2 Hz, 2H) (2 CH_2 of $SCNEt_2$); 5.70 (s, 1H), 5.85 (s, 2H) (3 CH of Tp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.84 (CH_3 of Tp*), 12.30 (2 CH_3 of Tp*), 12.88 (CH_3 of Tp*), 13.05 (CH_3 of $SCNEt_2$), 14.95 (CH_3 of $SCNEt_2$), 15.57 (2 CH_3 of Tp*), 44.16 (CH_2 of $SCNEt_2$), 52.24 (2 OCH_3), 54.11 (CH_2 of $SCNEt_2$), 105.95 (2 CH of Tp*), 107.13 (CH of Tp*), 141.34 (CMe of Tp*), 146.53 (2 CMe of Tp*), 158.93 (CMe of Tp*), 160.06 (2 CMe of Tp*), 163.18 (2 CO_2Me), 178.49 br (S*C*NEt_2), 193.0 br (C═C). Mass spectrum: *m/z* 717 (100% in peak cluster). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 534 sh (630), 684 (1025). Cyclic voltammetry (CH_2Cl_2, vs SCE): $E_{1/2} = +0.297$ V (reversible, Mo^V/Mo^{IV}).

Complex 2. Dimethyl acetylenedicarboxylate (0.1 mL, 0.8 mmol) was added to a solution of Tp*WS(S_2CNEt_2) (0.152 g, 0.231 mmol) in dichloromethane (30 mL), and the mixture was stirred for 18−24 h. The solvent was removed by rotary evaporation, and the residue was column chromatographed (silica gel, 1:10 CH_3CN:CH_2Cl_2). The purple fraction was collected, and its volume was reduced to near dryness. Methanol was added to the oily residue, and the volume again was reduced to produce black microcrystals. These were isolated by filtration and washed with methanol. Yield: 0.079 g, 43%.

Anal. Calcd for $C_{26}H_{38}BN_7O_4S_3W$: C, 38.87, H, 4.77; N, 12.20; S, 11.97. Found: C, 38.32; H, 4.87; N, 12.54; S, 12.33. Infrared (KBr): 2942 m, ν(BH) 2551 w, ν(C═O) 1727 and 1701 s, ν(CN) of Tp* 1545 s, ν(CN) of $SCNEt_2$ 1506 s, 1491 m, 1444 m, 1416 s, 1381 m, 1362 m, 1279 m, ν(C−O−C) 1232 vs, 1063 m, 1024 m, 853 w, 795 m, 689 w, 637 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.11 (t, ^3J 7.2 Hz, 3H), 1.32 (t, ^3J 7.2 Hz, 3H) (2 CH_3 of $SCNEt_2$); 1.91 (s, 3H), 2.23 (s, 3H), 2.61 (s, 6H), 2.84 (s, 6H) (6 CH_3 of Tp*); 3.88 (s, 6H, 2 CO_2CH_3); 4.43 (q, ^3J 7.2 Hz, 2H), 5.24 (q, ^3J 7.2 Hz, 2H) (2 CH_2 of $SCNEt_2$); 5.60 (s, 1H), 6.00 (s, 2H) (3 CH of Tp*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.55 (CH_3 of Tp*), 12.81 (2 CH_3 of Tp*), 15.03 (CH_3 of Tp*), 15.47 (CH_3 of $SCNEt_2$), 16.73 (CH_3 of $SCNEt_2$), 17.90 (2 CH_3 of Tp*), 44.13 (CH_2 of $SCNEt_2$), 52.40 (2 OCH_3), 54.32 (CH_2 of $SCNEt_2$), 107.87 (2 CH of Tp*), 108.72 (CH of Tp*), 142.29 (CMe of Tp*), 146.35 (2 CMe of Tp*), 160.35 (CMe of Tp*), 161.38 (2 CMe of Tp*), 167.17 (2 *C*O_2Me), 180.3 (C═C), 233.21 (S*C*NEt_2). Mass spectrum: *m/z* 801 (100% in peak cluster). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 390 sh (9620), 513 (1760), 594 sh (1155). Cyclic voltammetry (CH_2Cl_2, vs SCE): $E_{1/2} = +0.163$ V (quasi-reversible, W^V/W^{IV}).

Complex 3. Under anaerobic conditions, AgS_2CNEt_2 (0.223 g, 0.870 mmol) was added to a stirred solution of Tp*Mo$(CO)_3$I (0.516 g, 0.870 mmol) in acetonitrile (20 mL). After being stirred for 2 h, the reaction mixture was filtered, and the solids collected were extracted with dichloromethane to yield a khaki green solution. Reduction of the volume of the (filtered) extract to the point of incipient crystallization and addition of methanol yielded khaki green crystals of the product. Yield: 0.182 g, 35%.

Anal. Calcd for $C_{22}H_{32}BMoN_7O_2S_2$: C, 44.23; H, 5.40; N, 16.41; S, 10.73. Found: C, 43.85; H, 5.39; N, 16.10; S, 10.75. Infrared (CH_2Cl_2): ν(CO) 1974 and 1836 cm^{-1}. Infrared (KBr): 2971 w, 2929 w, ν(BH) 2551 w, ν(CO) 1978 s and 1812 vs, ν(CN) of Tp* 1545 m, ν(CN) of S_2CNEt_2 1498 m, 1431 m, 1417 m, 1373 m, 1357 m, 1283 m, 1203 m, 1149 m, 1084 w, 1067 m, 1043 w, 853 w, 796 w, 775 w, 694 w, 598 w, 497 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.27 (t, ^3J 7.2 Hz, 6H), 2.36 (s, 9H), 2.39 (s, 9H), 3.75 (q, ^3J 7.2 Hz, 4H), 5.84 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.4 MHz): δ 12.36 (2 CH_3 of S_2CNEt_2), 12.53 (3 CH_3 of Tp*), 14.75 (3 CH_3 of Tp*), 41.80 (2 CH_2 of S_2CNEt_2), 106.87 (3 CH of Tp*), 144.62 (3 CMe of Tp*), 152.92 (3 CMe of Tp*), 191.92 (S_2*C*NEt_2), 242.98 (2 CO). Electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 430 (3853), 645 (88).

Synthesis of Tp*MoS(S_2CNEt_2) from 3. A solution of **3** (0.119 g, 0.199 mmol) in dry, deoxygenated dichloromethane (15 mL) was treated with propylene sulfide (0.02 mL, 0.255 mmol) and then refluxed for 1 h under dinitrogen. The solution was allowed to cool, and the solvent was removed in vacuo. The residue was dissolved in a minimum volume of dichloromethane, filtered, and treated with methanol to precipitate yellow crystals of product. Yield: 0.070 g, 61%. Spectroscopic data of the product were identical to those reported in the literature (n.b. corrected electronic spectrum (CH_2Cl_2), λ nm (ϵ M^{-1} cm^{-1}): 485 sh (290), 1060 (56)).[32]

Synthesis of [Tp*Mo{$S_2C_2(CO_2Me)_2$}($SCNEt_2$)]PF_6. A solution of **1** (0.069 g, 0.096 mmol) in tetrahydrofuran (THF) was slowly treated with a THF:CH_3CN solution (7:1, 40 mL) of $[FeCp_2]PF_6$ and stirred for 1 h. An ESR-active species with $\langle g \rangle$ 1.974 was generated. Removal of the solvent in vacuo followed by trituration with *n*-hexane allowed the isolation of an air-sensitive, red-brown solid. Yield: 0.035 g, 42%.

Infrared (KBr): 2952 m, 2863 m, ν(BH) 2560 w, ν(C═O) 1732 and 1713 s, ν(CN) of $SCNEt_2$ 1580 m, ν(CN) of Tp* 1542 s, 1443 s, 1414 s, 1389 m, 1360 m, ν(C−O−C) 1242 vs br, 1144 m, 1111 m, 1077 m, 1038 m, 1023 m, PF_6^- 841 vs br, 691 w, 656 w, PF_6^- 558 s cm^{-1}.

Attempted Reaction of Tp*MO(S_2CNEt_2) and DMAC. Approximately 1.0 g of Tp*MO(S_2CNEt_2) (M = Mo, 0.18 mmol; W, 0.15 mmol) dissolved anaerobically in 1,2-$C_2H_4Cl_2$ was treated with DMAC (0.1 mL, 0.81 mmol) and refluxed for 5 and 4 days, respectively. Monitoring by thin-layer chromatography revealed no change in the reaction mixture; the starting materials were recovered in quantitative yield upon standard (vide supra) workup of the reactions.

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Table 1. Crystallographic Data for **1**−**3**

parameter	**1**·$0.75H_2O$	2	3
formula	$C_{26}H_{39.5}BMoN_7O_{4.75}S_3$	$C_{26}H_{38}BN_7O_4S_3W$	$C_{22}H_{33}BN_7MoO_2S_2$
fw	729.08	803.47	598.42
crystal system	orthorhombic	triclinic	triclinic
space group	*Pbcn*	$P\bar{1}$	$P\bar{1}$
a, Å	30.60(1)	12.219(2)	10.0501(2)
b, Å	13.764(3)	13.088(2)	10.1181(2)
c, Å	16.305(3)	11.403(2)	14.7404(3)
α, deg	90	102.23(1)	89.862(1)
β, deg	90	108.84(1)	82.038(1)
γ, deg	90	91.56(1)	62.051(1)
V, Å^3	6867(3)	1677.8(5)	1307.98(5)
Z	8	2	2
D_{calc}, g cm^{-3}	1.410	1.590	1.519
μ, cm^{-1}	6.08	36.71	6.94
unique reflns	7923	7733	5851
θ_{max}, deg	27.6	27.6	28.5
data with $I > n(I)$	$n = 2$, 3383	$n = 2$, 6077	$n = 3$, 4651
R	0.072	0.038	0.035
R_w	0.179	0.089	0.036
ρ_{max}, e Å^{-3}	0.68	1.05	0.73

Table 2. Interatomic Distances (Å) and Angles (deg) for **1** and **2**

atoms	**1** (M = Mo)	**2** (M = W)
M−S(1)	2.441(2)	2.3165(15)
M−S(2)	2.446(2)	2.4425(14)
M−S(3)	2.473(2)	2.3723(15)
M−N(11)	2.254(5)	2.294(4)
M−N(21)	2.222(6)	2.237(4)
M−N(31)	2.218(6)	2.225(5)
M−C(41)	2.106(8)	2.088(5)
S(1)−C(1)	1.748(8)	1.762(6)
S(2)−C(2)	1.749(9)	1.736(6)
S(3)−C(41)	1.657(9)	1.701(6)
C(1)−C(2)	1.340(11)	1.350(8)
N(1)−C(41)	1.280(10)	1.317(7)
S(1)−M−S(2)	85.20(7)	83.04(5)
S(1)−M−S(3)	82.19(9)	98.91(6)
S(2)−M−S(3)	80.00(10)	128.86(5)
S(3)−M−C(41)	41.5(2)	44.28(16)
M−S(1)−C(1)	100.8(3)	106.7(2)
M−S(2)−C(2)	100.0(3)	103.3(2)
M−S(3)−C(41)	57.3(3)	58.97(19)
M−C(41)−S(3)	81.2(4)	76.8(2)
M−C(41)−N(1)	147.8(7)	158.6(5)
S(3)−C(41)−N(1)	130.9(7)	124.0(5)
S(1)−C(1)−C(2)	123.8(6)	119.7(5)
S(2)−C(2)−C(1)	124.7(6)	122.4(5)

Table 3. Interatomic Distances (Å) and Angles (deg) for **3**

Distances			
Mo−S(1)	2.5379(7)	Mo−N(31)	2.197(2)
Mo−S(2)	2.5699(7)	S(1)−C(1)	1.701(3)
Mo−C(40)	2.039(3)	S(2)−C(1)	1.712(3)
Mo−C(50)	1.917(3)	C(40)−O(40)	1.151(3)
Mo−N(11)	2.227(2)	C(50)−O(50)	1.173(3)
Mo−N(21)	2.304(2)	C(1)−N(2)	1.312(3)

Angles			
S(1)−Mo−S(2)	67.19(2)	C(40)−Mo−N(21)	85.3(1)
S(1)−Mo−C(40)	128.57(8)	C(40)−Mo−N(31)	72.8(1)
S(1)−Mo−C(50)	98.23(8)	C(50)−Mo−N(11)	92.2(1)
S(1)−Mo−N(11)	77.49(6)	C(50)−Mo−N(21)	176.1(1)
S(1)−Mo−N(21)	81.61(6)	C(50)−Mo−N(31)	91.1(1)
S(1)−Mo−N(31)	154.04(6)	N(11)−Mo−N(21)	83.96(8)
S(2)−Mo−C(40)	68.22(8)	N(11)−Mo−N(31)	78.37(8)
S(2)−Mo−C(50)	79.67(8)	N(21)−Mo−N(31)	86.53(8)
S(2)−Mo−N(11)	141.94(6)	Mo−S(1)−C(1)	91.16(9)
S(2)−Mo−N(21)	103.77(6)	Mo−S(2)−C(1)	89.82(9)
S(2)−Mo−N(31)	138.47(6)	S(1)−C(1)−S(2)	111.8(2)
C(40)−Mo−C(50)	97.8(1)	Mo−C(40)−O(40)	175.5(2)
C(40)−Mo−N(11)	149.7(1)	Mo−C(50)−O(50)	178.2(2)

Crystal Structure Determinations. Crystals were grown by slow diffusion of methanol (for **1** and **3**) or hexanes (for **2**) into dichloromethane solutions of the complexes. Crystallographic data are reported in Table 1. Selected bond distances and angles are given in Tables 2 and 3.

Analysis of 1 and 2. Intensity data were measured at room temperature on a Rigaku AFC6R diffractometer fitted with Mo Kα radiation, $\lambda = 0.71073$ Å. Data were corrected routinely for Lorentz and polarization effects[35] as well as for absorption using an empirical procedure employing DIFABS.[36] The structures were solved by direct methods (SIR92[37]) and refined by a full-matrix least-squares procedure based on F^2.[38] Non-hydrogen atoms were refined with anisotropic displacement parameters, carbon-bound hydrogen atoms were included in the riding model approximation, and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, was applied: For **1**, $a = 0.1037$, $b = 0.131$; and **2**, $a = 0.0459$, $b = 1.5791$. Disorder was apparent in both **1** and **2**. In the case of **1**, two positions were resolved for the C(45) atom, and, from refinement, these were modeled with 50% site occupancy factors. The dynamic disorder evident in the molecule of **2** was not modeled. Two residual electron density peaks in **1**, each located on a crystallographic 2-fold axis and 2.78 Å apart, were modeled as water with O(2w) assigned half-weight, that is, sof = 0.25; hydrogen atoms were not included for these molecules. Thus, for each complex molecule, there are 0.75 equiv of lattice water with a total of six such molecules per unit cell. The latter molecules were located in the vicinity of the DMAC ligand, but well-defined interactions were not apparent. Figures 1 and 2 were prepared using ORTEP.[39]

Analysis of 3. Crystallographic data were collected at 123(1) K, on an Enraf-Nonius KappaCCD diffractometer system equipped with graphite monochromated Mo Kα radiation using ϕ with 1° frames, a detector to crystal distance of 29 mm, and a detector 2θ

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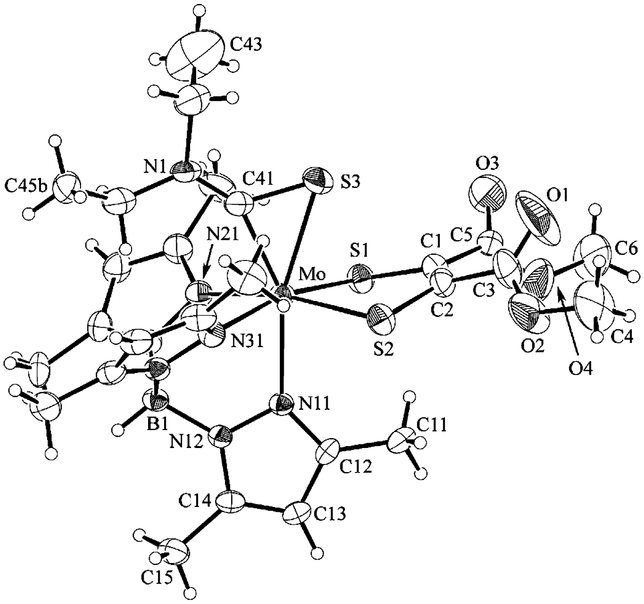

Figure 1. ORTEP diagram of **1** drawn at the 25% probability level. The numbering schemes of the pyrazole rings containing N(21) and N(31) parallel that shown for the ring containing N(11).

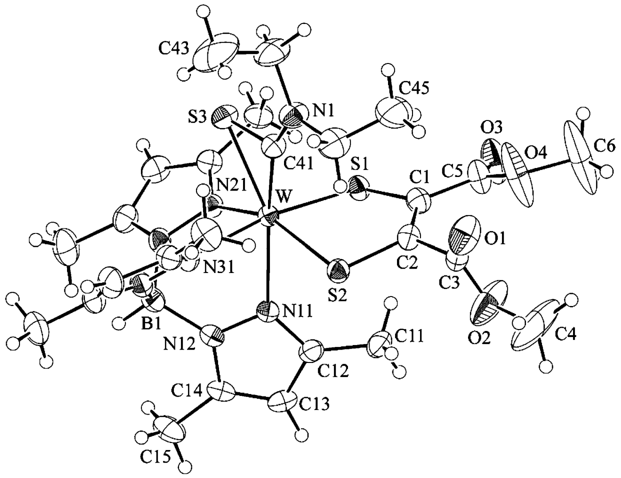

Figure 2. ORTEP diagram of **2** drawn at the 35% probability level. The numbering schemes of the pyrazole rings containing N(21) and N(31) parallel that shown for the ring containing N(11).

offset of −10.2° in ϕ. Absorption corrections were not applied. The final unit cell determination, scaling of the data, and corrections for Lorentz and polarization effects were performed with Denzo-SMN.[40] The structure was solved by direct methods (SIR92[37]), expanded with the Fourier technique (DIRDIF94[41]), and refined by the full-matrix least-squares method using the crystal structure analysis package teXsan[35] on a Silicon Graphics Indy computer.

All of the non-hydrogen atoms were located in the initial solution and refined anisotropically. The hydrogen atoms of the complex were included in the refinement at their calculated, geometrically constrained positions. Figure 3 was prepared using ORTEP.[39]

Results and Discussion

Synthesis and Characterization of 1 and 2. Air-stable, diamagnetic **1** and **2** were formed in the reactions of thio(dithiocarbamate) precursors with DMAC in dichloromethane at room temperature (eq 1). Due to the air-sensitivity of the starting material, **1** was prepared under anaerobic conditions, but similar precautions were unnecessary for the synthesis of **2**. Both complexes are soluble in chlorinated solvents, sparingly soluble in methanol, and insoluble in hydrocarbons and ether.

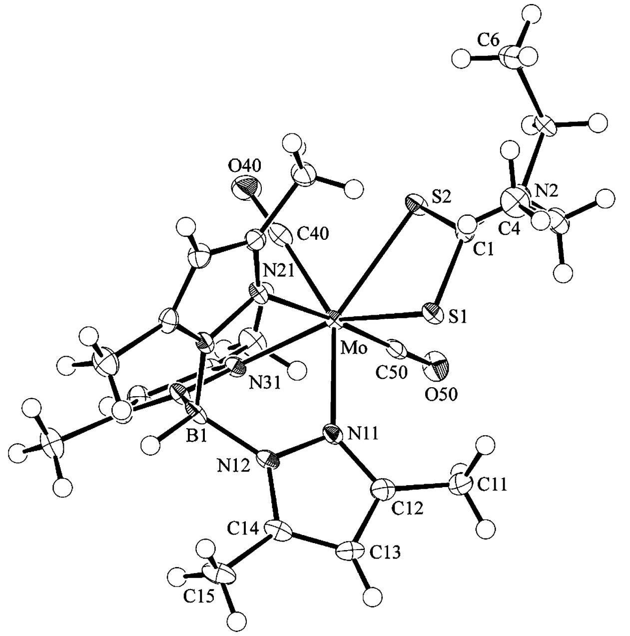

Figure 3. ORTEP diagram of **3** drawn at the 50% probability level. The numbering schemes of the pyrazole rings containing N(21) and N(31) parallel that shown for the ring containing N(11).

$$\mathrm{Tp^{*}MS(S_2CNEt_2) + MeO_2CC{\equiv}CCO_2Me \rightarrow Tp^{*}M\{S_2C_2(CO_2Me)_2\}(SCNEt_2)} \quad (1)$$

Possible mechanisms for the formation of **1** and **2** include nucleophilic attack on the alkyne by terminal thio or dithiocarbamate ligand sulfur atoms, followed by or in concert with attack of the incipient carbanion on the complementary sulfur-donor ligand. The observation that Tp*MO(S_2CNEt_2) (M = Mo,[32] W[33]) do not react with DMAC even under prolonged reflux at 90 °C provides indirect evidence for the involvement of the thio ligand in the reactions. Coucouvanis and co-workers have reported that terminal thio ligands are nucleophilic enough to attack DMAC.[42] Steric crowding at the metal center is likely to prevent the formation of a vinylsulfide-$\kappa S,C$ intermediate, although related vinyl disulfides are known.[42−44] The formation of an S-bound vinyl sulfide of the type recently reported

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by Maeyama et al. is a possibility.[45] There is no evidence of a long-lived species bearing the alkyne-coupled sulfur donor ligand *S*CR′═*C*R′SC(NEt$_2$)*S* (donors italicized, R′ = CO$_2$Me) described elsewhere.[31] Binding of the alkyne across both dithiocarbamate sulfur atoms followed by transfer of the C═NEt$_2^+$ fragment to the terminal thio ligand would appear unlikely, as the necessary approach is blocked by a Tp* methyl group. Unfortunately, we have been unable to detect or intercept any intermediates in the reactions.

Related reactions involving dithiocarbamate ligands have been implicated in dithiolene and “melded” ligand formation[29−31,46−49] and the generation of a thiocarboxamide tungstathiaenone complex in the reaction of Tp*W(S$_2$CNEt$_2$)(CO)$_2$ with DMAC.[50h] Thio complexes devoid of sulfur coligands react with alkynes to form thiametallacyclobutene species, the conversion of Cp*$_2$ZrS into Cp*$_2$Zr{SC(R)═C(R)} (R = Et, Ph, Tol) being a case in point.[51] Alkyne and terminal thio ligands are also known to coexist, for example, in Re(S)I(RC≡CR)$_2$ (R = Me, Et)[52] and WS(PhC≡CPh)(S$_2$CNEt$_2$)$_2$.[53] Treatment of the thio complexes WS(PhC≡CPh)(S$_2$CNR$_2$)$_2$ (R = Me, Et) with PEt$_3$ results in the abstraction of a sulfur atom and the formation of the thiocarboxamido complexes WS(PhC≡CPh)(SCNR$_2$)(S$_2$CNR$_2$).[50c] Surprisingly, and in contrast to the present situation, no dithiolene complexes are reported to form in any of these reactions.

Microanalytical and mass spectrometric data for **1** and **2** were consistent with the formulations. Infrared spectra exhibited peaks due to Tp* (ν(BH) ~2554 cm^{-1} and ν(CN) ~1546 cm^{-1}), carboxymethyl groups (ν(C═O) 1720, 1700 cm^{-1} and ν(C−O−C) 1230 cm^{-1}), and the thiocarboxamide ligand (ν(CN) 1497 and 1506 cm^{-1} for **1** and **2**, respectively). The latter are lower in energy than the ν(CN) modes of other group 6 thiocarboxamide complexes, which range from 1525 to 1573 cm^{-1}.[50] However, thiocarboxamido ν(CN) bands in the region 1490−1506 cm^{-1} have been reported for MS(SCNR$_2$)(S$_2$CNR$_2$)$_2$ (M = Nb, Ta) complexes.[54] The ^{1}H NMR spectra were consistent with molecular C_s symmetry in solution, with Tp* methyl and ring methine resonances having integrations of 6:6:3:3 and 2:1, respectively. A single OCH$_3$ resonance at ca. δ 3.9 was observed. The Tp* methyl resonances of **1** were ca. 0.4 ppm more deshielded than the corresponding resonances of **2**, but similar ethyl and methine resonances were observed for both compounds. Analogous spectra have been reported for Tp*Mo(NCS){S$_2$C$_2$(CO$_2$Me)$_2$}[16] and Tp*W(OPh){S$_2$C$_2$(CO$_2$Me)$_2$}.[17,18] Two triplet and two quartet resonances confirm the presence of inequivalent thiocarboxamide ethyl groups as a result of restricted rotation around the C═N bond. The very similar ^{1}H NMR data of **1** and **2**, in chloroform as well as other solvents (data not reported), are indicative of common solution structures. ^{13}C NMR spectra were also consistent with molecular C_s symmetry in solution. A resonance at δ 233.2 was assigned to the thiocarboxamide carbon in the W complex (confirmed by a gHMBC[55] cross-peak with the proximal methylene groups), a broad resonance at δ 178.5 being ascribed to the same carbon in the Mo complex (no gHMBC cross-peaks observed). The signals due to the dithiolenic carbon atoms could not be detected using routine ^{13}C NMR pulse sequences. However, very broad signals at δ 193.0 (Mo) and 180.3 (W) were observed with a 2 min pulse delay or shorter (3 vs 10 μs) receiver gain delays; the signals were not enhanced by the use of relaxation agents. The results of VT- and 2D-NMR experiments aimed at probing the orientation and dynamics of the thiocarboxamido ligands were inconclusive.

Complexes **1** and **2** underwent a one-electron oxidation (M^{V}/M^{IV}) at potentials of +0.297 and +0.163 V, respectively. Plots of I_{pa} versus $\nu^{1/2}$ were linear, and I_{pa}/I_{pc} ratios were close to unity for both complexes. A completely reversible process was observed for **1** with $E_{1/2}$ remaining constant at scan rates below 100 mV s^{-1}. The $E_{1/2}$ value varies slightly (up to −10 mV) at faster scan rates. Variation of ΔE_{pp} with scan rate was observed but only to the extent observed for the oxidation of internal ferrocene. Oxidation of **2** was quasi-reversible, with $E_{1/2}$ decreasing as scan rate increased. Ferrocenium oxidation of **1** produced an EPR-active species with $\langle g \rangle$ 1.974 and a hyperfine pattern typical of monomeric molybdenum species. The isolated hexafluorophosphate salt exhibited IR bands typical of Tp* (ν(BH) 2560 cm^{-1}, ν(CN) 1542 cm^{-1}), carboxymethyl groups (ν(C═O) 1732, 1713; ν(C−O−C) 1242 cm^{-1}), and PF$_6^-$ (841, 558 cm^{-1}). A medium-intensity peak at 1580 cm^{-1} was assigned to a thiocarboxamide ν(CN) vibration. The complex was tentatively identified as [Tp*Mo^{V}{S$_2$C$_2$(CO$_2$Me)$_2$}(SCNEt$_2$)]PF$_6$. Solutions of the complex were extremely air-sensitive, and attempts to grow diffraction-quality crystals were unsuccessful. Chemical oxidation of the tungsten analogue was not investigated.

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Synthesis and Characterization of 3. Discontinuation of commercial supplies of boron sulfide prompted the development of an alternative synthesis for Tp*MoS(S_2CNEt_2), originally prepared from Tp*MoO(S_2CNEt_2) and B_2S_3.[32] The new synthesis is based on sulfur atom transfer from propylene sulfide to Tp*Mo(S_2CNEt_2)$(CO)_2$, as described for the W analogue.[33] The dicarbonyl precursor was prepared by modification of a literature method for the synthesis of LMo(S_2CNEt_2)$(CO)_2$ [L = Tp, $HB(C_2H_2N_3)_3^-$, $PhB(C_2H_2N_3)_3^-$] from LMoI$(CO)_3$ and AgS_2CNEt_2 in acetonitrile.[56] Interestingly, the method reportedly failed to yield **3** when Tp*MoI$(CO)_3$ was reacted with AgS_2CNEt_2. In fact, coprecipitation of **3** and AgI led to the disposal of the complex by previous workers; extraction of the precipitated solids using dichloromethane allows ready separation of the complex from the silver salts.

Correct elemental analyses were obtained for samples of **3**. The IR spectrum of the compound contained bands characteristic of the Tp* (ν(BH) 2551, ν(CN) 1545 cm^{-1}) and dithiocarbamate (ν(CN) 1498 cm^{-1}) ligands. Two very strong ν(CO) bands at 1974 and 1835 cm^{-1} were observed in dichloromethane solutions. Similar ν(CO) bands at 1940 and 1815 cm^{-1} were observed for the W analogue[57] and the Mo complexes reported by Shiu et al.[56] ^{1}H and ^{13}C NMR spectra were consistent with fluxional behavior and effective C_{3v} symmetry on the NMR time scale (as observed for the W analogue). Three singlet resonances with an integrated intensity ratio of 3:9:9 were observed for the Tp* ligand, while triplet methyl and quartet methylene resonances were observed for the dithiocarbamate ligand. The room temperature ^{13}C NMR spectrum was also consistent with effective C_{3v} symmetry in solution. The S_2CN and carbonyl resonances were observed at δ 191.9 and 243.0, respectively. The dynamic processes involved were not probed.

Descriptions of Structures. Complexes **1** and **2** are seven-coordinate and possess tridentate *fac*-Tp*, bidentate dithiolene, and thiocarboxamido-$\kappa^2 S,C$ ligands bound to a central metal (M) atom. ORTEP views of **1** and **2** are shown in Figures 1 and 2, respectively, and selected bond distances and angles are collected in Table 2. The structures are closely related apart from the markedly different orientations adopted by the thiocarboxamido ligands (vide infra); we ascribe this difference in the structures to solid-state (packing and hydration) effects (n.b. the presence of common C_s solution structures according to ^{1}H NMR data).

Complex **1** exhibits a distorted octahedral geometry with the thiocarboxamido-$\kappa^2 S,C$ ligand occupying a single coordination site. The equatorial plane is defined by atoms S(1), S(2), N(21), and N(31), with atom displacements of 0.002(3), −0.002(3), −0.018(8), and 0.017(8) Å, respectively. The Mo atom is −0.2554(8) Å away from this plane, while the S(3)−C(41) midpoint and Mo and N(11) atoms define an angle of 177.3(5)°. The average 90° angle subtended by the vertices of the octahedron at Mo lends strong support to the octahedral description. The seven donor atoms of **1** do not map onto any of the common seven-coordinate geometries, viz., capped octahedral, capped trigonal prismatic, or pentagonal bipyramidal.[58] Related octahedral geometries have been reported for Tp*Mo(NCS)$\{S_2C_2(CO_2Me)_2\}$[16] and Tp*W(OPh)$\{S_2C_2(CO_2Me)_2\}$.[17,18]

The dithiolene ligand is symmetrically coordinated to the Mo center, with equivalent Mo−S distances averaging at 2.444(1) Å. Similar Mo−S distances have been reported for bent molybdocene mono(dithiolene) complexes,[24−26] but complexes such as Tp*Mo(NCS)$\{S_2C_2(CO_2Me)_2\}$ (av. 2.357(2) Å)[16] and $NEt_4[MoOX_2(S_2C_2Me_2)]$ (X = Cl (2.356(6) Å), S−Ad (2.393(2) Å))[27] are characterized by shorter Mo−S distances (as quoted above). The C(1)−C(2) bond distance of 1.340(11) Å is comparable to those reported for other complexes and is indicative of the presence of a double bond. The S_2C_4 fragment of **1** is nearly planar with a maximum atom deviation of 0.020(11) Å, but the Mo atom is −0.8395(6) Å out of this plane. The "envelope-like" fold of the dithiolene ligands is characterized by a dihedral angle of 24.3° between the S_2C_4 and MoS_2 planes. In Tp*Mo(NCS)$\{S_2C_2(CO_2Me)_2\}$, the Mo atom is −0.2376(9) Å out of the S_2C_4 plane and the ligand fold angle is only 7.8°.[16] Variations in the fold angle of dithiolene ligands may arise from steric or electronic interactions.[59]

The metrical parameters associated with the thiocarboxamido ligand are consistent with previous structures, except that the Mo−S(3) distance of 2.473(2) Å is significantly shorter than Mo−S bonds in monomeric (2.531(5)−2.626(1) Å)[50] and dimeric (2.517(2) Å[60] and 2.573(2) Å[61]) thiocarboxamido−Mo complexes. As a consequence of the short Mo−S(3) bond, the Mo−C(41)−S(3) bond angle of **1** (81.2(4)°) is more acute than those reported for related complexes (ca. 85°).[50] The $SCNC_2$ core of the ligand is planar with a maximum displacement of 0.09(1) Å for atom N(1). The thiocarboxamide ligand lies on the pseudo-mirror plane of the complex, with S(3) adjacent to the dithiolene sulfur atoms and the NEt_2 group projected back into a cleft in the Tp* ligand. The S(1)···S(3) and S(2)···S(3) distances of 3.230(4) and 3.162(4) Å, respectively, are inside the van der Waals separation of 3.6 Å for these atoms.[62]

Complex **2** exhibits a distorted pentagonal bipyramidal geometry. The pentagonal plane is defined by atoms S(2), S(3), N(11), N(21), and C(41), with displacements of −0.012(1), 0.013(1), 0.193(4), −0.191(4), and 0.044(5) Å, respectively, the axial positions by atoms S(1) and N(31). The central tungsten atom is −0.0682(2) Å out of the pentagonal plane, and the S(1)−W−N(31) angle is 170.72-

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(13)°. The M−S(dithiolene) distances are inequivalent, axial W−S(1) (2.3165(15) Å) being shorter than equatorial W−S(2) (2.4425(14) Å); the average W−S(dithiolene) bond distance of 2.384(1) Å in **2** is considerably longer than that of Tp*W(OPh){$S_2C_2(CO_2Me)_2$} (2.273(3) Å);[17] however, it is similar to the W−S bond distances of other tungsten mono(dithiolene) complexes (av. 2.39 Å).[21,22,46,63−66] Short W−S bonds are also characteristic of the PPh_4[Cp*WS(dithiolene)] complexes prepared by Tatsumi and co-workers (av. 2.326(2) Å).[21,22] Extended X-ray absorption fine structure (EXAFS) has also revealed short W−S(dithiolene) distances in *Clostridium thermoaceticum* formate dehydrogenase (2.39 Å)[67] and Tp*W(SePh){S_2C_2(Ph)(2-quin)} (2.31(2) Å).[18] The C(1)−C(2) bond distance of 1.350(8) Å in **2** is marginally longer than that of Tp*W(OPh){$S_2C_2(CO_2Me)_2$} (1.33(2) Å) but is comparable to other reported mono(dithiolene) C═C bond distances.[22,46,63−66] The dithiolene ligand in **2** is planar with a maximum atom displacement of −0.012(5) Å for C(1), with the metal −0.6176(2) Å out of this plane. The dihedral angle between the S_2C_4 and WS_2 planes is 20.3°. In comparison, the dithiolene S_2C_4 plane of Tp*W(OPh){$S_2C_2(CO_2Me)_2$} has a mean atom deviation of 0.035 Å and a dihedral angle of 8.7° with the WS_2 plane.[17]

The thiocarboxamide ligand framework ($SCNC_2$) of **2** is planar to 0.038 Å with a maximum displacement of 0.08(1) Å for atom N(1). Metrical parameters within the triangular WCS fragment include W−S(3) 2.3723(15) Å, W−C(41) 2.088(5) Å, and C(41)−S(3) 1.701(6) Å. The angles subtended at the W, S(3), and C(41) atoms are 57.3(3)°, 58.97(19)°, and 76.8(2)°, respectively. As for **1**, the W−S(3) distance in **2** is considerably shorter than other reported values in the literature, the average W−S distance of monomeric thiocarboxamido complexes being 2.562 Å.[50] The closest W−S bond distance (2.450(1) Å) is that reported for the cluster, $WCo_2(CO)_4(\mu\text{-}S)(\mu\text{-}SCNEt_2)(S_2CNEt_2)(PhC{\equiv}CPh)$, where the thiocarboxamido ligand bridges the three metal centers.[68] The C(41)−N(1) distance is 1.317(7) Å, the N atom adopting a trigonal planar geometry. Aminocarbyne character is indicated by the short W−C(41) distance and large W−C(41)−N(1) angle of 158.6(5)° (cf., for **1**, Mo−C(41)−N(1) = 147.5(9)°). The thiocarboxamide ligand is oriented so that the C(41)−S(3) and W−N(21) vectors are nearly coplanar, with S(3) adjacent to the pyrazole group containing N(21) and the NEt_2 group pointing away from Tp*.

The coordination geometry in **3** (see Figure 3 and Table 3) is also based on a pentagonal bipyramid, but the geometry is considerably more distorted than that of **2**. The central Mo atom is coordinated by tridentate Tp*, bidentate dithiocarbamate, and two terminal carbonyl ligands. The pentagonal plane is defined by atoms S(1), S(2), N(11), N(31), and C(40), leaving the N(21) and C(50) atoms to occupy the axial positions, with an N(21)−Mo−C(5) angle of 176.1(1)°. The deviations of the atoms from the least-squares pentagonal plane are −0.086(1), 0.085(1), 0.421(2), −0.105(3), and −0.727(4) Å, respectively. The Mo, N(21), and C(50) atoms lie 0.0002(4), −2.202(2), and 1.865(4) Å, respectively, out of the plane. The four-membered chelate ring formed by the almost symmetrically coordinated dithiocarbamate ligand is effectively planar with a mean deviation of 0.004 Å and forms a dihedral angle of 3.5° with the equatorial plane. There is a significant disparity in the Mo−C bond distances. Thus, the Mo−C(50) distance of 1.917(3) Å, with the C(50) atom trans to the N(21) atom, is shorter than the Mo−C(40) distance of 2.039(3) Å; the Mo−N(21) distance is the longer of the three W−N bonds. The steric demands of the Tp* ligand lead to an opening of the OC−M−CO angle in **3** (97.8(1)°) and its structurally related W analogue (97.5°)[57] as compared to the angles typical of complexes with sterically unencumbered scorpionate co-ligands (<75°).[56]

Concluding Remarks

The synthesis of mono(dithiolene) complexes from the reactions of terminal thio-metal complexes and alkynes is rare, with only two precedents to date.[17,22] The outcomes of the reactions are consistent with initial nucleophilic attack of the thio ligand on the alkyne followed by subsequent cleavage and sequestration of sulfur from the dithiocarbamate co-ligand. Similar mechanisms may attend the formation of dithiolene or melded ligand complexes in the reactions of alkynes and metal-dithiocarbamates.[29−31,46−49]

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Supporting Information Available: Crystallographic data for **1**, **2**, and **3** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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