Organometallics **2003,** *22,* 4853−4860

Product Diversity in the Reactions of $Tp^*W(S_2CNEt_2)(CO)_2$ with Alkynes: Novel η^2-Alkyne and Tungstathiaenone Complexes

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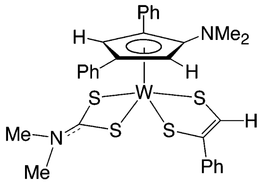
Received June 3, 2003

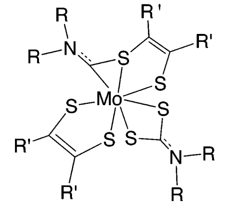
The reactions of $Tp^*W(S_2CNEt_2)(CO)_2$ [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate] with phenylacetylene, 2-butyne-1,4-diol, and dimethyl acetylenedicarboxylate (DMAC) in chlorinated solvents produce $Tp^*W(S_2CNEt_2\text{-}\kappa S)(\eta^2\text{-}PhC{\equiv}CH)(CO)$ (**1**), $Tp^*WCl(\eta^2\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)$ (**2**), and $Tp^*W\{OCC(CO_2Me){=}C(CO_2Me)S\text{-}\kappa^3O,C,S\}(SCNEt_2\text{-}\kappa^2C,S)$ (**3**), respectively. The complexes have been characterized by microanalysis, IR and ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and X-ray diffraction. Complexes **1** and **2** possess octahedral structures with aligned carbonyl and η^2-alkyne ligands (the latter occupying one coordination site) and a tridentate *fac*-Tp* ligand; the coordination spheres are completed by monodentate dithiocarbamate (W−S(1) 2.397(2) Å, W···S(2) 3.999(2) Å) and chloro ligands, respectively. Complex **3** contains a novel heterometallacycle incorporating acyl-κ^2O,C [ν(CO) 1585 cm^{-1}; δ_C (C=O) 269.2, $^1J_{CW}$ 18 Hz] and enethiolate units, a thiocarboxamido ligand [ν(CN) 1525 cm^{-1}; δ_C 250.3, $^1J_{CW}$ 81 Hz], and a tridentate *fac*-Tp* ligand. The complex exhibits an octahedral structure with planar, orthogonal acyl-enethiolate and thiocarboxamide ligands (the acyl and thiocarboxamide units each occupy one coordination site).

Introduction

The reactions of organic and organometallic species at metal−sulfur centers are of considerable current interest.[1,2] This interest is piqued by a desire for insights into the mechanism of industrial processes such as hydrodesulfurization[3] and the development of methods for the production of organosulfur compounds, ligands, and metal complexes with unique properties and technological applications, e.g., light- and redox-sensitive dithiolene complexes.[4]



(**A**)



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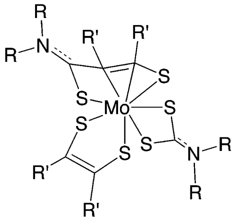

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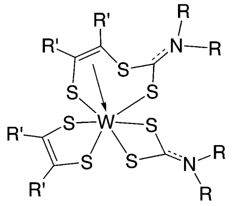

(**D**)

Although there are many stable organometallic sulfur-donor ligand complexes,[5−8] a significant number undergo intramolecular coupling, fragmentation, and/or rearrangement reactions producing novel organosulfur ligand complexes. Three examples highlight the unusual outcomes possible when alkynes react with dithiocarbamate complexes: (i) generation of the amidocyclopen-

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(2) *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.

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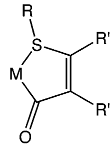
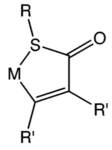
(5) Selected examples important in the context of this paper include $W(CO)(alkyne)(S_2CNR_2)_2$: (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318−1320. (b) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532−1538. (c) Templeton, J. L.; Herrick, R. S.; Morrow, J. R. *Organometallics* **1984**, *3*, 535−541. (d) Carlton, L.; Davidson, J. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2071−2076. $WX(CO)(S_2CNR_2)(alkyne)_2$: (e) Davidson, J. L.; Vasapollo, G. *J. Chem. Soc., Dalton Trans.* **1988**, 2855−2863. (f) Armstrong, E. M.; Baker, P. K.; Flower, K. R.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2535−2541. $[W(CO)L_{0-1}(S_2CNR_2)(alkyne)_2]^+$ (L = neutral N-donor): (g) Armstrong, E. M.; Baker, P. K. *J. Organomet. Chem.* **1988**, *352*, 133−140. (h) Baker, P. K.; Flower, K. R.; Drew, M. G. B. *Organometallics* **1993**, *12*, 276−282.

10.1021/om030416w CCC: $25.00

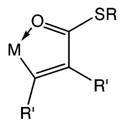
tadienyl complex **A** upon photolysis of $W(PhC{\equiv}CH)_2(S_2CNMe_2)_2$ in the presence of excess $PhC{\equiv}CH$,[9] (ii) formation of the melded ligand complexes **B** and **C** ($R' = CO_2Me$) in the reactions of $MoO(S_2)(S_2CNR_2)_2$, $[Mo_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]^{2+}$, or $Mo(S_2)(S_2CNR_2)_3$ with dimethyl acetylenedicarboxylate (DMAC),[10] and (iii) the production of **D** ($R' = CO_2Me$ or H/Ph) in the reactions of $WS(S_2)(S_2CNR_2)_2$ with DMAC or $PhC{\equiv}CH$ and their subsequent transformation into dithiolene complexes upon $S{-}C(S)NR_2$ bond cleavage and elimination of "$SCNR_2^{+}$".[11]



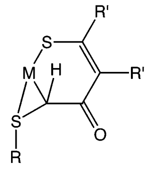
(**E**)



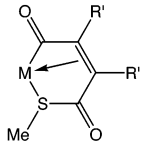
(**F**)



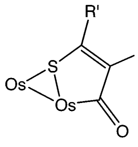
(**G**)



(**H**)

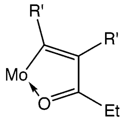


(**I**)

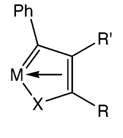


(**J**)

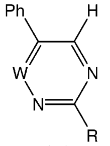
Heterometallacyclic complexes sometimes result from the reactions of alkynes with sulfur-donor and carbonyl ligands. For example, reactions of $CpM(SR)(CO)_3$ (M = Mo,[12] W[12−15]), $CpM(SR)(CO)_2$ (M = Fe,[14,16−18] Ru[19]), and $CpRu(SR)(CO)(PPh_3)$[19] with alkynes lead to complexes containing the five-membered heterometallacycles **E**, some of which undergo thermal or photochemical rearrangements ultimately producing species containing **F** or **G**, or π-alkyne complexes such as $CpW(SR)(\eta^2\text{-}R'C{\equiv}CR')(CO)$.[12−15,20] Six-membered heterometallacycles such as **H** and **I** are also produced in reactions of alkynes and $CpMo(SR)(CO)_3$ (or $[CpMo(CO)_3]_2$)[12,16] and $Fe(CO)_2(PMe_3)_2(\eta^2\text{-}HCS_2Me)$,[21] respectively. Related ligands are formed in multinuclear complexes; for example, reaction of $Os_3(CO)_9\{\mu_3\text{-}C_2CH_2C(Me)^tBu\}(\mu_3\text{-}S)$ with 30 equiv of $EtC{\equiv}CEt$ under UV irradiation leads to complexes containing the metallathiaenone **J** ($R' = Et$).[22] Heterometallacycle-bridged iron diphosphine complexes are also known.[23] None of these ligands contain the η^2-acyl unit often found in early transition metal phosphine,[24] cyclopentadienyl,[25] and bis-[26] and trispyrazolylborate[27] complexes.



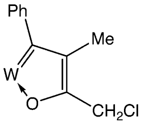
(**K**)



(**L**)



(**M**)



(**N**)

Heterometallacycle formation as a result of alkyne and co-ligand coupling is uncommon in group 6 metal trispyrazolylborate chemistry.[28] Examples include the reactions of $Tp^*Mo\{\eta^2\text{-}C(O)Et\}(CO)(NCMe)$ [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate] with alkynes under CO to produce the oxamolybdacycle **K**;[27c] related nioba- and tungstacycles **L** (X = O) are produced upon carbonylation of $Tp^*Nb(R)(OMe)(PhC{\equiv}CR')$ (R/R′ = Me/Ph)[29] or acidification of $Tp^*Nb(CO)(PhC{\equiv}CMe)_2$[30] and $Tp^*W(NPh)\{\eta^1\text{-}C(O)Me\}(PhC{\equiv}CMe)$.[28l] Alkynes are also known to couple with nitrile ligands producing metallacycle **M**, e.g., in the reaction of $[Tp^*W(PhC{\equiv}CH)(NCR)(CO)]BF_4$ with ammonia to produce $Tp^*W\{{=}C(Ph)C(H){=}N{-}C(R){=}N\}(CO)$ (R = Me, Ph).[28e] Protonation of

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(6) Organometallic sulfur-donor ligand W-Tp* complexes include $Tp^*W(S_2CNR_2)(CO)_2$: (a) Young, C. G.; Bruck, M. A.; Wexler, P. A.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.* **1992**, *31*, 587−593. $Tp^*W(SR)(CO)_2$: (b) Philipp, C. C.; Young, C. G.; White, P. S.; Templeton, J. L. *Inorg. Chem.* **1993**, *32*, 5437−5443. $Tp^*W(S_2PR_2)(CO)_2$: (c) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *J. Organomet. Chem.* **1998**, *560*, 1−6. Tp*WX(RCN)(CO) (X = anion): (d) Thomas, S.; Young, C. G.; Tiekink, E. R. T. *Organometallics* **1998**, *17*, 182−189. Tp*WSX(CO): (e) Thomas, S.; Tiekink, E. R. T.; Young, C. G. *Organometallics* **1996**, *15*, 2428−2430.

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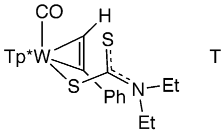
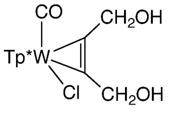
Tp*Nb(CO)(PhC≡CMe)(NCR) leads to the coupling of the alkyne and nitrile ligands to form **L** (X = NH).[30] Very recently, heterometallacycle **N** was identified in [Tp*W{=C(Ph)C(Me)=C(CH_2Cl)O}Cl]BAr_4, the product of the reaction of [Tp*W(CO)(OEt_2)(PhC≡CMe)]BAr_4 [Ar = 3,5-bis(trifluoromethyl)phenyl] with dichloromethane; the heterometallacycle is formed upon coupling of alkyne, carbonyl, and dichloromethanide fragments.[31] Related species are minor products of the photochemical reactions of Tp*W$(CO)_3$H with alkynes.[27e]



(**1**)



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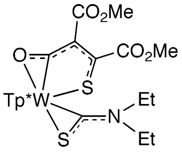

(**3**)

In this paper we describe the reactions of Tp*W(S_2CNEt_2)$(CO)_2$ with phenylacetylene, 2-butyne-1,4-diol, and DMAC. The observed products, Tp*W(S_2CNEt_2-κS)(η^2-PhC≡CH)(CO) (**1**), Tp*WCl(η^2-$HOCH_2C{\equiv}CCH_2OH$)(CO) (**2**), and Tp*W{OCC(CO_2Me)=C(CO_2Me)S-κ^3*O,C,S*}(SCNEt$_2$-κ^2*C,S*) (**3**), respectively, indicate that the dithiocarbamate ligand is an active participant in the reactions, undergoing dechelation, solvent-assisted dissociation, or desulfurization, producing a novel tungstathiaenone moiety, depending on the alkyne involved.

Results and Discussion

Syntheses and Characterization. The reactions of Tp*W(S_2CNEt_2)$(CO)_2$ with phenylacetylene, 2-butyne-1,4-diol, or DMAC in refluxing 1,2-dichloroethane produce emerald green **1**, sky-blue **2**, or purple-blue **3**, respectively. In the formation of **1**, a classical side-on-bonded, four-electron-donor alkyne ligand displaces a carbonyl ligand and a sulfur donor atom of the dithiocarbamate; a second, blue compound isolated upon chromatography has been tentatively characterized as Tp*WCl(η^2-PhC≡CH)(CO) (the analogue of **2**), formed by reaction of **1** with eluent (CH_2Cl_2). Replacement of carbonyl and dithiocarbamate ligands by a four-electron-donor alkyne and a solvent-derived[32] chloride ion (possibly via an analogue of **1**) occurs during the formation of **2** (eq 1). Tractable products, including **2**, were not formed when the reaction was performed in toluene. Iodo complexes related to **2** have been extensively studied by Templeton and co-workers,[28] but **2** appears to be the first chloro carbonyl alkyne trispyrazolylborate complex of W(II) to be reported.

$$2\text{Tp*W}(S_2CNEt_2)(CO)_2 + 2HOCH_2C{\equiv}CCH_2OH + ClCH_2CH_2Cl \rightarrow 2\ \mathbf{2} + [Et_2NC(S)SCH_2-]_2 + 2CO \qquad (1)$$

The formation of **3** may involve the formation of an η^2-alkyne intermediate like **1**, followed by concerted nucleophilic attack (and cleavage) of the dithiocarbamate ligand on the alkyne and of the “alkyne” β-carbon on the carbonyl ligand. η^2-Acyl complexes are now relatively common, especially for the oxophilic early transition (and group 8) metals.[24−27] However, the combination of η^2-acyl and enethiolate moieties in a chelating ligand is unprecedented.

Microanalytical and mass spectrometric data ([**1** − CO]$^+$ *m/z* 731, [**2**]$^+$ *m/z* 630, [**3**]$^+$ *m/z* 799) for the compounds were consistent with the formulations. Infrared spectra exhibited bands due to Tp* [ν(BH) ca. 2550 cm^{-1}, ν(CN) ca. 1545 cm^{-1}] and the complementary ligands. Thus, **1** exhibited ν(CO) and phenylacetylene ν(C≡C) bands at 1918 (strong) and 1652 cm^{-1} (weak), respectively. A strong band at 1474 cm^{-1} and a pair of weak bands at 1006 and 982 cm^{-1} were assigned to the ν(CN) and ν(CS) modes, respectively, of the dithiocarbamate ligand; the 24 cm^{-1} difference in the ν(CS) bands is indicative of monodentate coordination.[33] Bands at 1475, 1005, and 987 cm^{-1} have been assigned to the monodentate dithiocarbamate ligand of Tp*Mo(S_2CNEt_2-κ^2*S,S′*)(S_2CNEt_2-κ*S*).[34] The spectrum of **2** exhibited a strong ν(CO) band at ca. 1912 cm^{-1} and alkyne ν(OH) and ν(C≡C) bands at 3379 and ca. 1640 (weak) cm^{-1}, respectively. The presence of the thiocarboxamide ligand in **3** was indicated by a ν(CN) band at 1525 cm^{-1}. Reported thiocarboxamide ν(CN) bands in other mononuclear Mo and W complexes range from 1524 to 1573 cm^{-1}.[35] No metal−carbonyl ν(CO) band was observed; however, a weak band at 1585 cm^{-1} was assigned to the ν(CO) mode of the side-on-bonded acyl unit. This is within the narrow range observed for η^2-acyl trispyrazolylborate complexes of Mo and W (1490−1510 cm^{-1})[27] and the considerably broader range reported for all Mo/W η^2-acyl complexes (1425−1695 cm^{-1}).[24−27] The presence of carboxymethyl groups (from DMAC) was indicated by ν(C=O) bands at 1726 and 1705 cm^{-1} and a strong ν(C−O−C) band at 1226 cm^{-1}.

The room-temperature ^{1}H NMR spectrum of **1** revealed broad peaks in the δ 3.4−4.7 region, indicative

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of fluxional behavior at this temperature. However, the spectrum at 233 K was consistent with the presence of a single isomer of C_1 symmetry (see Experimental Section). The alkyne proton at δ 13.43 showed two-bond coupling of 6 Hz to tungsten, consistent with other tungsten phenylacetylene complexes of Tp*.[28] The room-temperature ^{13}C NMR spectrum of **1** confirmed C_1 symmetry. Notable resonances identified the presence of terminal carbonyl (δ 231, $^{1}J_{CW} = 147$ Hz), four-electron-donor phenylacetylene (δ 192 and 201, $^{1}J_{WC} = 49$ Hz)[7,28] and monodentate dithiocarbamate (δ 209)[36] ligands.

The ^{1}H NMR spectra of **2** were also consistent with fluxional behavior at room temperature but the presence of a C_1 symmetric species at low temperature (see Experimental Section). The hydroxyl protons undergo exchange, as indicated by the broad room-temperature resonance from δ 4.5 to 5.2. At 203 K, this resonance splits into two broad signals centered at δ 4.60 and 6.16. One set of CH_2 protons appeared as a broad doublet of doublets (δ 4.50 and 5.55), while the other set appeared as a doublet at δ 5.33. ^{13}C NMR spectroscopy confirmed the C_1 symmetry of the complex and the ligands present. The Tp* methyl carbons appeared as a broad resonance (δ 12.62) equivalent to three carbons and three relatively sharp signals from δ 15.7 to 16.1. The Tp*-*C*H and Tp*-*C*Me signals appeared as three and six singlets, respectively. Broad signals at δ 67 and 70 and δ 200 and 209 were assigned to the methylene and alkyne carbon atoms of the four-electron-donor 2-butyne-1,4-diol ligand.[7]

The inequivalence of all Tp* methyl and methine resonances in the ^{1}H and ^{13}C NMR spectra of **3** is indicative of molecular C_1 symmetry. In the ^{1}H NMR spectrum, overlapping triplets and corresponding multiplets were assigned to the methyl and diastereotopic methylene protons, respectively, of the thiocarboxamido ligand. Two singlets due to the $-CO_2Me$ groups were observed. The methyl groups of the thiocarboxamido ligand (δ(^{13}C) 12.24 and 14.39) were distinguished from the methyl groups of Tp* with the aid of gHMQC experiments. Correlations were also observed between the methoxy protons and the $-CO_2Me$ atoms of DMAC, as well as the Tp* methyl protons and the pyrazolyl ring carbons. Notably, there were no correlations to the peaks assigned to the acyl and enethiolate carbons (vide infra). In the ^{13}C NMR spectrum of **3**, the resonance at δ 250 ($^{1}J_{CW} = 81$ Hz) was assigned to the thiocarboxamido carbon; the resonance is within the literature range of δ 227−263 expected for this ligand.[35] HMBC results corroborated this assignment. The resonance at δ 269 ($^{1}J_{WC} = 18$ Hz) was assigned to the acyl carbon atom. It is in the chemical shift range typical of side-on-bonded acyls (δ 250−288), but the coupling constant is smaller than values reported for related carbonyl/nitrosyl cyclopentadienyl complexes (66−77 Hz).[25] The signals at δ 120 ($^{2}J_{WC} = 8$ Hz) and δ 177 were assigned to the alkene carbon atoms bonded to sulfur and carbon, respectively. The CO_2Me resonance at δ 165 also shows a significant long-range coupling (12 Hz) to the metal center. Full assignment of the spectra (see Experimental Section) was assisted by gHMQC and HMBC experiments.

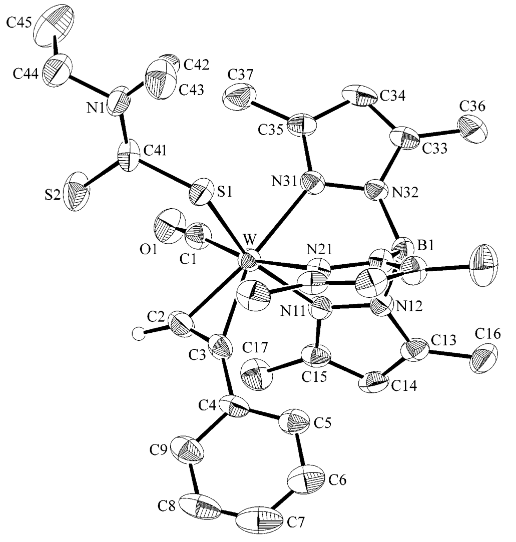

Figure 1. Molecular structure of **1** showing the atom-labeling scheme. The labeling of the pyrazole ring containing N(21) follows that shown for the rings containing N(11) and N(31). Hydrogen atoms, with the exception of C(2)-H, have been omitted for clarity, and thermal ellipsoids are shown at the 35% probability level.

Table 1. Selected Bond Distances and Angles for 1

distance (Å)		angle (deg)	
W−S(1)	2.397(2)	W−C(1)−O(1)	174.7(5)
W···S(2)	3.999(2)	S(1)−W−C(1)	97.2(2)
W−N(11)	2.214(4)	S(1)−W−C(2)	101.7(2)
W−N(21)	2.253(5)	S(1)−W−C(3)	104.45(10)
W−N(31)	2.225(4)	S(1)−C(41)−S(2)	120.9(4)
W−C(1)	1.975(7)	N(11)−W−N(21)	85.6(2)
W−C(2)	2.031(5)	N(11)−W−N(31)	77.4(1)
W−C(3)	2.046(5)	N(21)−W−N(31)	81.9(2)
S(1)−C(41)	1.798(7)	N(21)−W−C(1)	168.2(2)
S(2)−C(41)	1.668(6)	C(2)−W−C(3)	36.8(3)
N(1)−C(41)	1.334(7)	C(2)−C(3)−C(4)	138.1(5)
C(1)−O(1)	1.147(9)	C(3)−C(2)−H(2)	144
C(2)−C(3)	1.288(10)	W−C(2)−H(2)	144
C(2)−H(2)	1.09	W−C(3)−C(4)	148.7(4)

Crystal Structure of 1. The structure of **1** in its 1,2-dichloroethane solvate is displayed in Figure 1, and selected bond lengths and angles are presented in Table 1. The complex possesses a distorted octahedral coordination sphere defined by terminal carbonyl, monodentate dithiocarbamate, π-bonded phenylacetylene (occupying one site), and tridentate Tp* ligands. The carbonyl, phenylacetylene, and dithiocarbamate ligands are mutually *cis* by virtue of the *facial* coordination of Tp*. The alkyne C(2)−C(3) and carbonyl C(1)−O(1) units are roughly parallel, as measured by a C(1)−W−C(2)−C(3) torsion angle of 12.0(3)°. Consequently, the W(CO)(C≡C) unit is close to being planar (mean deviation 0.069 Å). The orientation of the alkyne parallel to the W−C≡O unit optimizes bonding interactions between alkyne $\pi_{\perp}$, alkyne $\pi_{\parallel}$*, and carbonyl π* orbitals and matching metal d orbitals.[7] However, exact alignment of the alkyne and carbonyl units is prevented by steric conflicts between the alkyne and pyrazolyl units. Further, this steric conflict manifests itself in the canting of the pyrazolyl rings about the pseudo-3-fold

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axis of the Tp*W unit. This is particularly noticeable in the ring containing N(11), which is canted by approximately 13° from its nominal position (in a mirror plane of a C_{3v} unit). The W($HC{\equiv}CC_{ipso}$) unit is not perfectly planar, as seen in the W−C(2)−C(3)−C(4) torsion angle of −169.2(6)°. This distortion allows the phenyl ring to position itself centrally between the pyrazolyl rings containing N(11) and N(21).

The alkyne ligand adopts the familiar *cis* bent structure upon coordination, the W−C(3)−C(4), W−C(2)−H(2), C(2)−C(3)−C(4), and C(3)−C(2)−H(2) angles being 148.7(4)°, 144°, 138.6(5)°, and 144°, respectively. The W−C(2/3) bond distances are short at an average of 2.038(4) Å, consistent with a four-electron-donor alkyne. The C(2)−C(3) distance is 1.288(10) Å. While the M−C bond distance is a good indicator of electronic structure, there are no significant differences in the C−C bond distances (1.28 ± 0.02 Å) of two-, three-, and four-electron-donor alkyne ligands.[7] The W−C(2) bond (2.031(5) Å) proximal to the carbonyl ligand appears shorter, although not significantly, than the W−C(3) bond (2.045(5) Å). All of these observations are characteristic of carbonyl alkyne complexes.[7,28] The four-electron-donor phenylacetylene ligand in [Tp*W(CO)($PhC{\equiv}CH$)($NH{=}C(Me)NH_2$)]BF_4[28e] is closely related to that of **1**, with W−C_{alkyne} distances of 2.040(7) (proximal to CO) and 2.011(8) Å and a $C_{ipso}{-}C{\equiv}C$ bond angle of 138.2(7)°. The carbonyl ligand is unremarkable, with typical bond distances and angles of W−C(1) = 1.975(7) Å, C(1)−O(1) = 1.147(9) Å, and W−C(1)−O(1) = 174.7(5)°.

The structural parameters of the monodentate dithiocarbamate ligand are in accord with those of related group 6 complexes.[34,38,39] The W−S(1) distance of 2.397(2) Å is typical of W−S single bonds, while the W···S(2) distance of 3.999(2) Å is just inside the estimated van der Waal's contact distance for these atoms.[38] The uncoordinated sulfur atom is positioned atop the octahedral face defined by the non-Tp* ligands (proximal to the metal) but well clear of the alkyne and carbonyl units. The monodentate coordination mode results in disparate C(41)−S(1) and C(41)−S(2) distances of 1.798(7) and 1.668(6) Å, respectively, the shorter being associated with a C=S unit. The dithiocarbamate unit is pushed toward the pyrazole ring containing N(21) by a neighboring lattice solvent molecule, the shortest C(51/52)−S_{dithio} distances being in the range 3.9−4.0 Å. In the only other structurally characterized monodentate dithiocarbamate complex of tungsten, viz., CpW(S_2CNMe_2)$(CO)_3$, W−S, W···S, C−S, and C=S distances of 2.496(1), 3.905(1), 1.769(3), and 1.676(3) Å, respectively, are observed.[38]

Structure of 2. The structure of **2** in its dichloromethane solvate, along with the atom-labeling scheme, is shown in Figure 2. Selected bond lengths and angles are presented in Table 2. The distorted octahedral coordination sphere is made up of tridentate Tp*, carbonyl, chloro, and η^2-$HOCH_2C{\equiv}CCH_2OH$ ligands (the alkyne occupies one vertex of the octahedron). As in **1**, the alkyne C≡C unit lies roughly parallel to the W−C≡O axis (C(1)−W−C(3)−C(2) torsion angle = 10.0(3)°) and the W(CO)(alkyne) unit is close to planar. As stated, this arrangement optimizes π-interactions between the ligand and metal orbitals.[7] Steric interactions between the pyrazole groups and the alkyne are again evident from a significant canting (ca. 9°) of the pyrazolyl ring containing N(11) from the pseudo-3-fold axis of Tp*. The carbon atoms of the alkyne unit are planar (mean deviation = 0.024 Å), and the C(5)−C(2)−C(3) and C(2)−C(3)−C(4) angles are 140.0(4)° and 139.3(5)°, respectively. These values are comparable to other reported tungsten(II) complexes of Tp* containing carbonyl, alkyne, and iodide ligands.[28] The C≡C bond distance of 1.316(6) Å and the W−C_{alkyne} bond distances of 2.016(5) and 2.039(5) Å are consistent with the presence of a four-electron-donor alkyne.[7] The W−C(3) bond proximal to the carbonyl ligand is longer than the distal W−C(2) bond, as observed for Tp*WI($PhC{\equiv}CMe$)(CO), Tp*WI{$PhC{\equiv}CCHMeCH(OH)Ph$}(CO), and Tp*WI(cyclodecyne)(CO).[28]

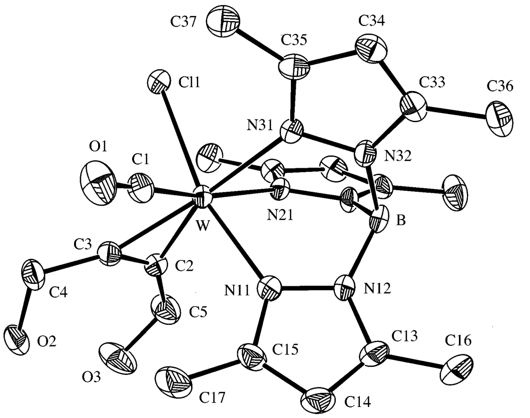

Figure 2. Molecular structure of **2** showing the atom-labeling scheme. The labeling of the pyrazole ring containing N(21) follows that shown for the rings containing N(11) and N(31). Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances and Angles for 2

distance (Å)		angle (deg)	
W−Cl(1)	2.449(1)	Cl(1)−W−C(1)	91.1(1)
W−N(11)	2.169(4)	N(11)−W−N(21)	85.6(1)
W−N(21)	2.231(4)	N(11)−W−N(31)	80.9(1)
W−N(31)	2.244(4)	N(21)−W−N(31)	80.8(1)
W−C(1)	1.956(5)	N(21)−W−C(1)	167.6(2)
W−C(2)	2.016(5)	C(2)−W−C(3)	37.9(2)
W−C(3)	2.039(5)	W−C(1)−O(1)	177.8(4)
O(1)−C(1)	1.165(6)	C(3)−C(2)−C(5)	140.0(4)
C(2)−C(3)	1.316(6)	C(2)−C(3)−C(4)	139.3(5)

The carbonyl ligand (W−CO = 1.956(5) Å, W−C(1)−O(1) = 177.8(4)°) is unremarkable, and the chloro ligand is characterized by a W−Cl(1) distance of 2.449(1) Å, within expectations. The complex represents a rare example of chloro ligation *cis* to both carbonyl and alkyne ligands (a feature of the more numerous organometallic iodo complexes of Tp*[28]). The structure of W($HC{\equiv}COAlCl_3$)(CO)$(PMe_3)_3$Cl, where the chloro ligand is *trans* to the alkyne and *cis* to the carbonyl ligand (W−Cl = 2.476(1) Å), is more typical. In all cases, the W−Cl bond distance is longer than the observed distance for **2**.

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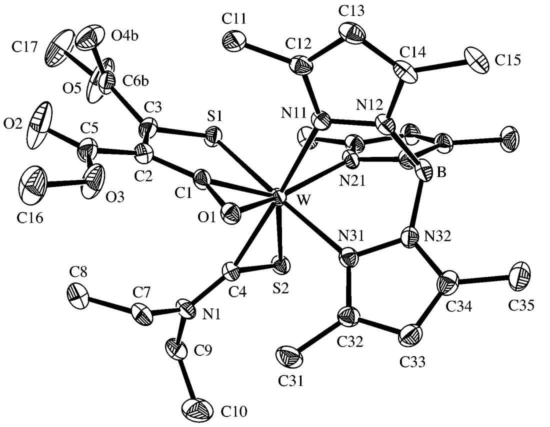

Figure 3. Molecular structure of **3** showing the atom-labeling scheme. The labeling of the pyrazole ring containing N(21) follows that shown for the rings containing N(11) and N(31). Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are shown at the 20% probability level.

Table 3. Selected Bond Distances and Angles for 3

Distances (Å)

W−O(1)	2.132(4)	W−C(1)	1.970(6)	W−S(1)	2.4733(18)
W−S(2)	2.5040(16)	W−C(4)	2.096(7)	W−N(11)	2.254(5)
W−N(21)	2.276(5)	W−N(31)	2.229(6)	O(1)−C(1)	1.268(8)
C(1)−C(2)	1.417(10)	C(2)−C(3)	1.395(11)	C(3)−S(1)	1.698(7)
S(2)−C(4)	1.695(7)	C(4)−N(1)	1.317(9)		

Angles (deg)

O(1)−W−C(1)	35.7(2)	W−C(1)−C(2)	137.2(6)
O(1)−W−S(1)	107.37(14)	O(1)−C(1)−C(2)	142.6(6)
O(1)−W−S(2)	125.72(13)	C(1)−C(2)−C(3)	109.3(6)
O(1)−W−C(4)	85.1(2)	W−S(1)−C(3)	104.5(3)
C(1)−W−S(1)	71.6(2)	S(1)−C(3)−C(2)	116.7(6)
C(1)−W−S(2)	123.2(2)	W−S(2)−C(4)	56.0(2)
C(1)−W−C(4)	84.3(3)	W−C(4)−S(2)	81.9(3)
S(1)−W−S(2)	86.10(6)	W−C(4)−N(1)	151.9(6)
S(1)−W−C(4)	87.8(2)	S(2)−C(4)−N(1)	125.8(6)
S(2)−W−C(4)	42.1(2)	N(11)−W−N(21)	75.21(19)
W−O(1)−C(1)	65.1(3)	N(11)−W−N(31)	84.2(2)
W−C(1)−O(1)	79.1(4)	N(21)−W−N(31)	88.8(2)

Both hydroxyl-H atoms form H bonds in the structure of **2**. The O(3)−H forms an intramolecular H bond to the O(2) hydroxyl group so that H···O(2) is 1.81 Å, O(2)···O(3) is 2.792(5) Å, and the angle at the H atom is 167°. The O(2)−H forms a H bond with the chloro ligand so that H···Cl(1)^i is 2.09 Å, O(3)···Cl(1)^i is 3.104(3) Å, and the angle subtended at H is 170° for symmetry operation i: $0.5 - x$, $-0.5 + y$, $0.5 - z$. These latter interactions serve to connect the complex species into a zigzag chain mediated by H-bonding contacts.

Crystal Structure of 3. Complex **3** exhibits the octahedral structure shown in Figure 3; selected bond distances and angles may be found in Table 3. The coordination sphere is comprised of a facial tridentate Tp* ligand, a thiocarboxamido-κ^2*C,S* ligand, and a novel, chelating acyl-enethiolate-κ^3*O,C,S* ligand incorporated into a tungstathioenone heterometallacycle. The thiocarboxamide and acyl units each occupy one coordination site in the octahedral description.

The thiocarboxamide ligand framework ($WSCNC_2$) is essentially planar with a mean atomic deviation of 0.039 Å. Metrical parameters within the triangular WCS fragment include the following: W−S(2) 2.5040(16) Å, W−C(4) 2.096(7) Å, C(4)−S(2) 1.695(7) Å. The angles subtended at the W, S(2), and C(4) atoms are 42.1(2)°, 56.0(2)°, and 81.9(3)°, respectively. These parameters are consistent with the few data available for structurally characterized mononuclear thiocarboxamido-W complexes.[35] The C(4)−N(1) distance is 1.317(9) Å, the N atom adopting a trigonal-planar geometry. Aminocarbyne character is indicated by the short W−C(4) distance and large W−C(4)−N(1) angle of 151.9(6)°. The thiocarboxamide ligand is orientated such that the C(4)−S(2) and W−N(21) vectors are nearly coplanar and so that S(2) is directed toward the pyrazole group containing N(21), while the NEt_2 group is directed away from it.

The novel acyl-enethiolate ligand is chelated to the W center via atoms C(1), O(1), and S(1), the heterometallacyclic unit [W,O(1),C(1)−C(3),S(1)] being essentially planar with a mean atom deviation of 0.032 Å. There is a small envelope-like bend along the C(1)···S(1) vector, producing a dihedral angle of 6° between the W,C(1),S(1) and C(1)−C(3),S(1) planes. A dihedral angle of only 1.0° relates the W,C(1),S(1) and W,C(1),O(1) planes. The carboxymethyl group containing C(5) is coplanar with the heterometallacycle, the torsional angle O(2)−C(5)−C(2)−C(3) being 1.6°. The second carboxymethyl group is disordered and twisted out of the heterometallacycle plane by ca. 40° (as measured by the torsion angles O(4a/b)−C(6a/b)−C(3)−C(2)). The triangular W,C(1),O(1) unit is broadly typical of related units that have been structurally characterized. The W−C(1) and W−O(1) distances of 1.970(6) and 2.132(4) Å, respectively, are both at the lower end of the observed ranges in related η^2-acyl complexes (1.96−2.21 and 2.16−2.30 Å, respectively).[24−27] The angles within the triangular WCO fragment are comparable with previous determinations.[24−27] However, the C(1)−W−O(1) angle of 35.7(2)° is opened by the closer approach of the CO unit to W. Moreover, the O(1)−C(1)−C(2) unit is more linear than commonly observed, the O(1)−C(1)−C(2) and W−C(1)−C(2) angles of 142.6(6)° and 137.2(6)°, respectively, being well outside typical values (ranging from 121° to 128° and 146° to 158°, respectively). The C(1)−C(2) and C(2)−C(3) bond distances are statistically equivalent at 1.37(1) Å, the distance being only slightly longer than a typical C=C double bond.[40] The C(3)−S(1) distance of 1.698(7) Å lies between expectations for C−S single (1.75 Å) and C=S double bonds (1.67 Å).[40] The W−S(1) bond of 2.4733(18) Å is longer than the mean value derived from arenethiolate structures (2.41 Å). The structural parameters are all consistent with electronic delocalization within the ligand framework. The acyl-enethiolate ligand is reminiscent of the thioketene ligand observed in TpMoO{SCC(*p*-tol)C(O)S-κ^3*C,S,S′*}, prepared by Hill et al.[41] This ligand is also planar due to electronic delocalization along the ligand backbone.

The η^2-acyl and thiocarboxamido units are orthogonal to one another, as measured by the dihedral angle of 88.4° between the W,C(1),O(1) and W,C(4),S(2) planes. The W,C(4),S(2) plane is orientated to bisect the O(1)−W−C(1) angle. The projection of the thiocarboxamido NEt_2 group over the η^2-acyl group of the chelating acyl-enethiolate ligand results in the displacement of the acyl unit from the “equatorial” W,S(1),N(21),N(31) plane and the tilting of the metallacycle with respect to that plane; the midpoint of the C(1)−O(1) vector is 0.91 Å out of

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the "equatorial" plane, the dihedral angle between the ligand and "equatorial" planes being 23.2°.

Summary

The reactions of $\mathrm{Tp^*W(S_2CNEt_2)(CO)_2}$ with phenylacetylene, 2-butyne-1,4-diol, and DMAC produce a variety of products **1**−**3**. The reaction with phenylacetylene produces a four-electron-donor π-alkyne carbonyl complex featuring a rare monodentate dithiocarbamate ligand, **1**. A similar complex is envisaged to form in the reaction with 2-butyne-1,4-diol, but the enhanced nucleophilicity or facile dissociation of the dithiocarbamate results in its replacement by a solvent-derived chloride ligand in **2**. The formation of **3** may also involve a transient monodentate dithiocarbamate complex that undergoes nucleophilic attack (and cleavage) of the dithiocarbamate ligand on the alkyne with concomitant nucleophilic attack of the "alkyne" β-carbon on a carbonyl ligand. The η^2-acyl-enethiolate and associated tungstathiaenone moieties have not been previously described. The complexes are related by a continuum of transformations, all involving the dithiocarbamate coligand but apparently controlled by the electrophilicity of the incoming or coordinated alkyne. The results underscore the need to examine a range of reactant combinations in order to completely define the reactions of alkynes with sulfur-donor ligand complexes.

Experimental Section

Materials and Methods. Unless otherwise stated, all reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk line techniques. Samples of $\mathrm{Tp^*W(S_2CNEt_2)(CO)_2}$ were prepared by the method of Young et al.[6a] Alkynes were purchased from Aldrich Chemical Co. and used as received. Infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained using Varian FT Unity300, Unity Plus 400, or INOVA400WB spectrometers and were referenced to internal $\mathrm{CHCl_3}$ (^{1}H δ 7.26, ^{13}C δ 77.0). High-resolution mass spectra were recorded using a Bruker BioApex 47e STMS fitted with an Analytica electrospray source. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA.

$\mathrm{Tp^*W(S_2CNEt_2\text{-}\kappa \mathit{S})(\eta^2\text{-}PhC{\equiv}CH)(CO)}$ (1). A mixture of $\mathrm{Tp^*W(S_2CNEt_2)(CO)_2}$ (0.202 g, 0.295 mmol) and phenylacetylene (0.1 mL, 0.910 mmol) in 1,2-$\mathrm{C_2H_4Cl_2}$ (15 mL) was refluxed for 3 h, whereupon the solution turned bright green. The solvent was removed in vacuo and the residue chromatographed on a silica gel column using dichloromethane as eluent. The blue-green fraction was collected, treated with hexanes, and evaporated to dryness to yield green product. Yield: 0.060 g, 27%. Anal. Calcd for $\mathrm{C_{29}H_{38}BN_7OS_2W{\cdot}0.75CH_2Cl_2}$: C, 43.41; H, 4.84; N, 11.91; S, 7.79. Found: C, 43.30; H, 4.83; N, 11.63; S, 7.71. IR (KBr): 2959 m; 2926 m; 2858 m; ν(BH) 2549 m; ν(CO) 1918 vs; ν(C≡C) 1652 w; ν(CN) of Tp*, 1545 m; ν(CN) of $\mathrm{S_2CNEt_2}$, 1474 m; 1446 m; 1413 m; 1368 m; 1302 w; 1261 m; 1206 s; 1132 m; 1068 m; 1045 m; ν(C=S), 1006 m and 982 m; 916 w; 859 w; 819 m; 783 m; 753 m; 694 m; 645 w; 562 w; 454 w cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$, 233 K): δ 1.06 (t, 3H, ^3J 7.5 Hz, $\mathrm{CH_2C\mathit{H}_3}$ A), 1.32 (t, 3H, ^3J 7.5 Hz, $\mathrm{CH_2C\mathit{H}_3}$ B); 1.61, 1.75, 2.35, 2.46, 2.56, 2.57 (s, 3H, 6 $\mathrm{C\mathit{H}_3}$ of Tp*); 3.40 and 4.28 (each dq, total 2H, ^2J 15 Hz, ^3J 7.5 Hz, diastereotopic $\mathrm{C\mathit{H}_2CH_3}$ A); 3.66 and 4.68 (each dq, total 2H, ^2J 15 Hz, ^3J 7.5 Hz, diastereotopic $\mathrm{C\mathit{H}_2CH_3}$ B); 5.63, 5.84, 5.89 (s, 1H, 3 C*H* of Tp*); 6.63−7.16 (m, Ph); 13.43 (s, 1H, $^2J_{\mathrm{HW}}$ 6 Hz, =C*H*). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 298 K): δ 12.2 br (2 $\mathrm{CH_2\mathit{C}H_3}$), 12.6, 12.8, 12.9, 15.3, 15.6, 15.9 (6 $\mathrm{\mathit{C}H_3}$ of Tp*), 48−51 br (2 $\mathrm{\mathit{C}H_2CH_3}$), 106.9, 107.5, 108.5 (3 *C*H of Tp*), 128.0, 129.4, 137.2 (Ph), 143.9, 144.2, 144.4, 149.0, 154.2, 154.9 (6 *C*Me of Tp*), 192.4 (C=*C*H), 201.2 ($^1J_{\mathrm{CW}}$ 49 Hz, C=*C*Ph), 209.33 ($\mathrm{S_2\mathit{C}NEt_2}$), 230.6 ($^1J_{\mathrm{CW}}$ 147 Hz, *C*O). MS, *m*/*z* (% in multiplet): 728 (34), 729 (86), 730 (80), 731 (100), 732 (63), 733 (66), 734 (34), $[\mathrm{M - CO}]^+$.

$\mathrm{Tp^*WCl(\eta^2\text{-}HOCH_2C{\equiv}CCH_2OH)(CO)}$ (2). A mixture of $\mathrm{Tp^*W(S_2CNEt_2)(CO)_2}$ (0.275 g, 0.401 mmol) and 2-butyne-1,4-diol (0.127 g, 1.48 mmol) in 1,2-$\mathrm{C_2H_4Cl_2}$ (20 mL) was refluxed for 3 h. The solvent was removed in vacuo and the residue taken up in a minimum volume of $\mathrm{CH_2Cl_2}$ and eluted down a silica gel column using 1:10 $\mathrm{CH_3CN{-}CH_2Cl_2}$ as eluent. Yellow, orange, and khaki green bands were collected before the blue-green band containing **2**. The blue-green fraction was evaporated to dryness to yield light blue microcrystals. The product was recrystallized by enriching a dichloromethane solution with *n*-hexane. Yield: 0.095 g, 38%. Anal. Calcd for $\mathrm{C_{20}H_{28}BClN_6O_3W{\cdot}CH_2Cl_2}$: C, 35.25; H, 4.23; N, 11.75; Cl, 14.87. Found: C, 35.20; H, 4.23; N, 11.75; Cl, 14.94. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1909 cm^{-1}. IR (KBr): ν(OH) 3379 s br; 2966 w; 2926 m; 2859 w; ν(BH) 2554 m; 2014 w; ν(CO) 1912 vs; ν(C≡C) 1640 w; ν(CN) 1546 s; 1448 s; 1417 s; 1384 s; 1367 s; 1209 s; 1068 s; 1034 s; 861 m; 819 m; 786 m; 739 m; 694 m; 643 m; 467 w br cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K): δ 1.65, 2.28, 2.32, 2.44, 2.49, 2.80 (each s, 3H, 6 $\mathrm{C\mathit{H}_3}$ of Tp*), 4.50 (d, 1H, ^2J 18 Hz, $\mathrm{C\mathit{H}_2}$), 4.5−5.2 (br, 2H, 2 O*H*), 5.33 (d, 2H, ^2J 18 Hz, $\mathrm{C\mathit{H}_2}$), 5.55 (d, 1H, ^2J 18 Hz, $\mathrm{C\mathit{H}_2}$), 5.74, 5.81, 5.99 (each s, 1H, C*H* of Tp*). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 203 K): δ 1.53, 2.15, 2.28, 2.36, 2.43, 2.69 (each s, 3H, 6 $\mathrm{C\mathit{H}_3}$ of Tp*), 4.41 (d, 1H, ^2J 18 Hz, $\mathrm{C\mathit{H}_2}$), 4.60 (br, 1H, O*H*) 5.24 (d, 2H, ^2J 18 Hz, $\mathrm{C\mathit{H}_2}$), 5.47 (d, ^2J 18 Hz, $\mathrm{C\mathit{H}_2}$), 5.72, 5.88, 6.03 (each s, 1H, 3 C*H* of Tp*), 6.16 (br, 1H, O*H*). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 12.6 (br, 3 $\mathrm{\mathit{C}H_3}$), 15.7, 15.8, 16.1 (3 $\mathrm{\mathit{C}H_3}$), 67.3, 69.8 (br, 2 $\mathrm{\mathit{C}H_2}$), 107.4, 107.9, 108.0 (3 *C*H), 143.6, 144.4, 145.5, 150.3, 153.2, 154.2 (6 *C*Me), 200.8, 209.1 (br, *C*≡*C*), 231.8 ($^1J_{\mathrm{WC}}$ 146 Hz, *C*O).

$\mathrm{Tp^*W\{OC(CO_2Me){=}C(CO_2Me)CS\text{-}\kappa^3\mathit{O,C,S}\}(SCNEt_2\text{-}\kappa^2\mathit{C,S})}$ (3). A solution of $\mathrm{Tp^*W(S_2CNEt_2)(CO)_2}$ (0.502 g, 0.733 mmol) in 1,2-$\mathrm{C_2H_4Cl_2}$ (30 mL) was treated with DMAC (0.15 mL, 1.220 mmol), then refluxed for 3 h. Alternatively, the reaction may be carried out by stirring at room temperature for 5 days. The deep blue mixture was evaporated to dryness in vacuo, and the residue was taken up in a minimum volume of $\mathrm{CH_2Cl_2}$, then passed through a silica gel column using 1:23 $\mathrm{CH_3CN{-}CH_2Cl_2}$ as eluent. Blue crystals were isolated by either slow evaporation or cooling (−4 °C) of an ether solution of the product. Yield: 0.178 g, 30%. Complex **3** is highly soluble in most solvents with the exception of water. Anal. Calcd for $\mathrm{C_{27}H_{38}BN_7O_5S_2W}$: C, 40.57; H, 4.79; N, 12.27. Found: C, 40.01; H, 4.90; N, 11.71. IR (KBr): 2943 m; ν(BH) 2557 m; ν(C=O) of DMAC 1726 s, 1705 s; ν(C=O) 1585 w; ν(CN) of Tp* 1547 s; ν(CN) of $\mathrm{SCNEt_2}$ 1525 m; 1439s; 1415 s; 1383 m; 1365 m; 1297 m; 1278 m; ν(C−O−C) 1226 vs; 1193 m sh; 1150 m; 1072 m; 1048 m; 1002 m; 944 w; 909 w; 874 m; 856 m; 812 m; 790 m; 776 m; 738 w; 696 m; 653 m; 644 m; 484 w cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.08, 1.10 (each t, 3H, ^3J 7.2 Hz, 2 $\mathrm{CH_2C\mathit{H}_3}$), 1.56, 2.14, 2.22, 2.40, 2.47, 2.83 (each s, 3H, 6 $\mathrm{C\mathit{H}_3}$ of Tp*), 3.1−3.8 (m, 4H, 2 $\mathrm{C\mathit{H}_2CH_3}$), 3.87, 3.94 (each s, 3H, 2 $\mathrm{OC\mathit{H}_3}$), 5.49, 5.94, 5.96 (each s, 1H, 3 C*H* of Tp*). ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 12.2, 14.4 (2 $\mathrm{CH_2\mathit{C}H_3}$), 12.6, 12.8, 13.0, 13.4, 13.6, 18.1 (6 $\mathrm{\mathit{C}H_3}$ of Tp*), 45.2, 54.8 (2 $\mathrm{\mathit{C}H_2CH_3}$), 51.7, 52.7 (2 $\mathrm{O\mathit{C}H_3}$), 108.3, 108.7, 109.9 (3 *C*H of Tp*), 119.7 ($^2J_{\mathrm{WC}}$ 8 Hz, WS*C*(R)=C(R)), 143.3, 143.9, 144.4, 152.6, 154.2, 156.4 (6 *C*Me of Tp*), 164.4 ($\mathrm{\mathit{C}O_2Me}$), 165.1 ($^3J_{\mathrm{WC}}$ 12 Hz, $\mathrm{\mathit{C}O_2Me}$), 177.3 (WC(O)*C*(R)=C(R)), 250.3 ($^1J_{\mathrm{WC}}$ 81 Hz, $\mathrm{S\mathit{C}NEt_2}$), 269.2 ($^1J_{\mathrm{WC}}$ 18 Hz, W*C*(O)). MS *m*/*z* (% in multiplet): 797 (61), 798 (85), 799 (100), 800 (56), 801(92).

Crystallography. Structure of $\mathbf{1{\cdot}C_2H_4Cl_2}$. Emerald green crystals of **1**·$\mathrm{C_2H_4Cl_2}$ were grown by slow diffusion of *n*-hexane into a 1,2-dichloroethane solution of the complex. Data for a crystal 0.07 × 0.10 × 0.25 mm^3 in dimensions were collected at room temperature on a CAD4 diffractometer fitted with Mo Kα radiation (λ 0.70169 Å) using the $\omega{-}2\theta$ scan technique.

Table 4. Crystallographic Data

	1·$C_2H_4Cl_2$	**2**·CH_2Cl_2	**3**
formula	$C_{31}H_{42}BCl_2N_7OS_2W$	$C_{21}H_{30}BCl_3N_6O_3W$	$C_{27}H_{35}BN_7O_5S_2W$
fw	858.41	714.52	796.40
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	12.665(2)	10.4264(2)	13.2648(6)
b (Å)	12.771(2)	14.8083(2)	12.0920(5)
c (Å)	13.480(4)	17.6029(4)	23.1805(10)
α (deg)	73.13(2)	90	90
β (deg)	64.19(2)	101.045(1)	91.95(1)
γ (deg)	74.93(1)	90	90
V (Å^3)	1855.6(7)	2667.50(8)	3716.0(3)
Z	2	4	4
ρ_{calc} (g cm^{-3})	1.536	1.772	1.424
T (K)	293	150	293
μ (mm^{-1})	3.407	4.671	3.262
no. of measd reflns	6795	43836	22915
θ_{max} (deg)	25.0	30.1	27.5
no. of unique reflns	6490	7727	8390
no. of reflns, $I > 3.0\sigma(I)$	5403	5586	7219, $I > 2.0\sigma(I)$
no. of refined params	386	326	419
R	0.042	0.038	0.044
R_w	0.051	0.038	0.164 (all data)

Data were corrected for Lorentz and polarization effects and for absorption using an empirical procedure.[42] Crystallographic data are collected in Table 4. The structure was solved by heavy-atom methods[43] and refined on F.[44] For the complex, non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in their calculated positions except for the alkyne-bound H(2) atom, which was located from a difference map. A solvent molecule of 1,2-dichloroethane included in the lattice was disordered, as evidenced by large thermal motion; multiple sites were not found for the constituent atoms. The atoms comprising this molecule were refined isotropically. Refinement converged to R 0.042 and R_w 0.051 after the application of a weighting scheme of the form $1/[\sigma^2(F)]$. The maximum residual electron density peak in the final difference map (3.44 e Å^{-3}) was located in the vicinity of the disordered solvent molecule. Figure 1 was prepared using ORTEP.[45]

Structure of 2·CH_2Cl_2. Blue rods of **2**·CH_2Cl_2 were grown by slow diffusion of *n*-hexane into a dichloromethane solution of the complex. Data for a crystal 0.08 × 0.13 × 0.25 mm^3 in dimensions were collected at 150(1) K on an Enraf-Nonius KappaCCD diffractometer system equipped with Mo Kα radiation using ϕ and ω rotations with 1° frames, a detector to crystal distance of 29 mm, and a detector 2θ offset of $-10.2°$ in ϕ and $-6.6°$ in ω. 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.[46] The structure was solved by direct methods (SIR92[47]), expanded with the Fourier technique (DIRDIF94[43]), and refined by the full-matrix least-squares technique using the crystal structure analysis package teXsan[44] on a Silicon Graphics Indy computer. Crystallographic data are summarized in Table 4.

All of the non-hydrogen atoms of the tungsten complex were located in the initial solution and refined anisotropically. The hydrogen atoms of the complex were included in the refinement at their geometrically constrained positions. One of the chlorine atoms of the dichloromethane of crystallization was disordered over two sites, Cl(2A) and Cl(2B). Each site was refined as a partially occupied chlorine atom with the sum of their site occupancies constrained to one. Figure 2 was prepared using ORTEP.[45]

Structure of 3. Deep purple-black crystals of **3** were grown with difficulty by slow diffusion of water into a thf solution of the complex; a crystal of dimensions 0.08 × 0.35 × 0.40 mm^3 was selected for data collection. Intensity data were collected with a Bruker SMART Apex CCD detector using Mo Kα radiation (graphite crystal monochromator $\lambda = 0.71073$).[48] Accurate cell parameters and crystal orientation were obtained by least-squares refinement of 8900 reflections with θ values between 2.3° and 24.7°, respectively. Data were reduced using the program SAINT and corrected for absorption (ratio of max./min. transmission 0.67).[48] Crystallographic data are summarized in Table 4.

The structure was solved by direct methods and difference Fourier synthesis.[48] Hydrogen atoms were included in calculated positions. Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. The refinement converged with conventional R $[I > 2\sigma(I)]$ and R_w (all data) of 0.044 and 0.164. The weighting scheme employed was of the type $w = [\sigma^2(F_o^2) + (0.093P)^2 + 8.55P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. In the final difference map the maximum and minimum peak heights were 2.39 and -0.83 e Å^{-3}, respectively. Figure 3 was prepared using ORTEP.[45]

Acknowledgment. We thank Mr. Hassan Akhlaghi and Dr. Andrew Millar for experimental assistance and Dr. Gary Fallon for use of an X-ray diffractometer at Monash University. We gratefully acknowledge the Australian Agency for International Development for a studentship to P.J.L. and the University of Melbourne and the National University of Singapore (Grant R-143-000-151-112) for financial support.

Supporting Information Available: Details of the structure determinations including atomic coordinates, bond distances and angles, and thermal parameters. This information is available free of charge via the Internet at http://pubs.acs.org.

OM030416W

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