Synthesis and Structure of $W(\eta^2\text{-mp})_2(CO)_3$ (mp = Monoanion of 2-Mercaptopyridine) and Its Reactions with 2,2′-Pyridine Disulfide and/or NO To Yield $W(\eta^2\text{-mp})_4$, $W(\eta^2\text{-mp})_2(NO)_2$, and $W(\eta^2\text{-mp})_3(NO)$

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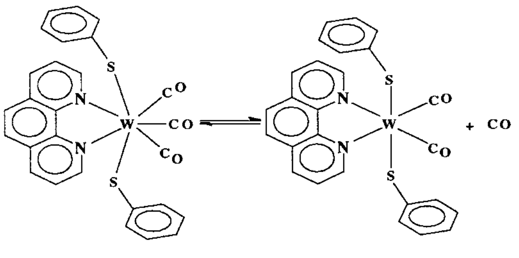
Oxidative addition of the sulfur−sulfur bond of 2,2′-pyridine disulfide ($C_5H_4NS{-}SC_5H_4N$) with $L_3W(CO)_3$ [L = pyridine, $^1/_3$CHPT; CHPT = cycloheptatriene] in methylene chloride solution yields the seven-coordinate W(II) thiolate complex $W(\eta^2\text{-mp})_2(CO)_3$ (mp = monoanion of 2-mercaptopyridine). This complex undergoes slow further oxidative addition with additional pyridine disulfide, yielding $W(\eta^2\text{- mp})_4$. Reaction of $W(\eta^2\text{-mp})_2(CO)_3$ with NO results in quantitative formation of the six-coordinate W(0) complex $W(\eta^2\text{-mp})_2(NO)_2$. Reaction of $W(\eta^2\text{-mp})_2(CO)_3$ with NO in the presence of added pyridine disulfide yields the seven-coordinate W(II) nitrosyl complex $W(\eta^2\text{-mp})_3(NO)$ as well as $W(\eta^2\text{-mp})_2(NO)_2$ and trace amounts of $W(\eta^2\text{-mp})_4$. The complex $W(\eta^2\text{-mp})_3(NO)$ is formed during the course of the reaction and not by reaction of $W(\eta^2\text{-mp})_4$ or $W(\eta^2\text{-mp})_2(NO)_2$ with NO under these conditions. The crystal structures of $W(\eta^2\text{- mp})_2(CO)_3$, $W(\eta^2\text{-mp})_2(NO)_2$, and $W(\eta^2\text{-mp})_3(NO)$ are reported.

Introduction

Oxidative addition of disulfides is an important route to preparation of metal thiolate complexes.[1] As part of our interest in physical studies of metal/sulfur complexes,[2,3] we report the study of oxidative addition of phenyl disulfide to the W(0) complex:

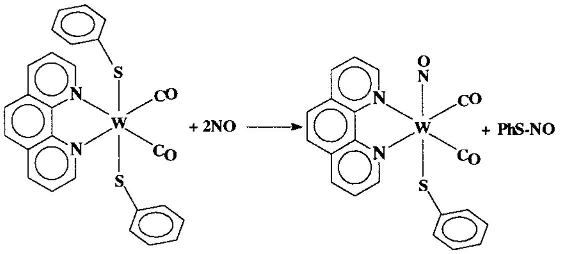
$$W(phen)(CO)_3(EtCN) + PhS{-}SPh \rightarrow W(phen)(CO)_3(SPh)_2 \quad (1)$$

The coordinatively saturated W(II) complex was observed to rapidly and reversibly bind CO:



(2)

The dicarbonyl complex reacted with NO via reductive elimination[4] of PhSNO:



(3)

Reaction of an analogous thiolate complex $W(phen)(CO)_2(\eta^2\text{-}S,S{-}arene)$ in which the sulfur atoms were part of a chelating arene disulfide ligand indicated different reactivity[4] and prompted the current studies using 2-mercaptopyridine as a chelating ligand.

For the group VI metals, several investigators have reported complexes relevant to this work. Abrahamson[5] reported the preparation of $CpW(CO)_3(\eta^1\text{-mp})$ as well as its decarbonylation [reactions 4 and 5 occurring with visible and UV light respectively]:

$$[CpW(CO)_3]_2 + PyS{-}SPy \xrightarrow{h\nu} 2(\eta^1\text{-mp})W(CO)_3Cp \quad (4)$$

$$(\eta^1\text{-mp})W(CO)_3Cp \xrightarrow{h\nu} (\eta^2\text{-mp})W(CO)_2Cp + CO \quad (5)$$

In addition, Deeming and co-workers have investigated the reaction of $W(CO)_3(MeCN)_3$ and pyridine-2-thione to give low yields of a dichelate $W(\eta^2\text{-mp})_2(CO)_3$ as well as $W(\eta^1\text{-mp})(CO)_5$ byproduct.[6] The crystal structure of a stable phosphine-substituted seven-coordinated complex $W(\eta^2\text{-mp})_2(PMe_2Ph)(CO)_2$ was also reported. A similar complex, $W(\eta^2\text{-mpd})_2(CO)_3$

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(mpd = monoanion of 2-mercaptopyrimidine), was prepared by Baker and co-workers[7] from the reaction of $WI_2(CO)_3(NCMe)_2$ and K[mpd], and its crystal structure was reported.

Further chelation of the N,S moiety was demonstrated by Cotton and Ilsley[8] who prepared the eight-coordinate complex W(η^2-mpd)$_4$. Zubieta and co-workers extended this work by reporting a number of complexes derived from 2-mercaptopyridine, 2-mercaptopyrimidine, and related ligands[9] [M = Mo, W]:

$$MCl_4(thf)_2 + 4H\text{-mpd} \xrightarrow{[base]} M(\eta^2\text{-mpd})_4 \qquad (6)$$

The crystal structures of both eight-coordinate M(IV) thiolate products show bidentate coordination of each of the thiopyrimidine ligands. This degree of coordinative saturation is in contrast to the four-coordinate tetrahedral structure of Mo(S−t-Bu)$_4$, a related M(IV) tetrathiolate that does not have chelating donor ligands.[10] Also noteworthy is that these chelating S,N donor complexes bear a resemblance to the well-developed chemistry of the dithiocarbamate ligand, a monoanionic ligand with S,S donor atoms.[11]

2,2′-Pyridine disulfide presents a good system for study because its chelating properties allow it to form four-membered ring complexes that may be subject to steric strain. Earlier thermochemical investigations showed that strain energies on the order of 10 kcal/mol were present in four-membered ring systems involving metal complexes of chelating diphosphines and that this strain nearly vanished for five- and six-membered rings.[12] For the chelating 2-thiopyridine ligand, the presence and magnitude of ring strain as well as its possible chemical consequences remain largely an open question. Flood and co-workers[13] have recently reported the study of reactions of *mer*-(PMe$_3$)$_3$Os(H)(η^2-O−Py) in which ring strain was implicated.

This paper reports syntheses and structures of several thiopyridine complexes of tungsten. It is part of a long-term goal to understand the physical chemistry of the metal−sulfur bond in organometallic complexes. The synthetic and structural studies described here are the basis for detailed kinetic and thermodynamic studies in progress, which will be reported later.

Experimental Section

General. All manipulations were performed under an argon atmosphere using standard Schlenk tube and glovebox techniques. Solvents were purified and degassed using standard procedures. Infrared spectra were obtained in sealed solutions cells on a Perkin-Elmer 2000 FTIR spectrophotometer. NMR spectra were obtained on a Bruker AVANCE 300 MHz NMR spectrometer using septa-fitted tubes from Wilmad Scientific and were solvent-calibrated. 2,2′-Pyridine disulfide was obtained from Aldrich Chemical and used without further purification. Nitric oxide was obtained from Matheson gas and purified by passing though a copper trap maintained at −78 °C to remove NO_2/N_2O_4. Research grade carbon monoxide was obtained from Matheson gas and was used without further purification. Elemental analyses were performed by Galbraith Laboratories, Inc. Mass spectra were obtained on a VG MASSLAB TRIO-2 spectrometer using FAB of methylene chloride solutions.

Preparation of (η^2-mp)$_2$W(CO)$_3$. In a glovebox 4.04 g of (CHPT)W(CO)$_3$ (0.0112 mol; CHPT = cycloheptatriene) and 2.50 g of pyridine disulfide (0.0113 mol) were weighed into a 100 mL round-bottom flask. To this flask was added approximately 100 mL of CH_2Cl_2, and the contents were stirred overnight. The reaction was monitored by FTIR, and the bands of the starting material at 1981, 1908, and 1872 cm^{-1} decreased over a period of several hours as the bands of the product at 2022 and 1928 cm^{-1} increased. After about 7 h the reaction was judged essentially complete and the solution was filtered to remove any solid materials. After addition of 25 mL of heptane, the solution was filtered through a short Celite column and stored in the freezer overnight. An amount of 0.43 g of the first crop of crystals was isolated. The filtrate was concentrated, and additional heptane was added. Storage in the freezer for several hours yielded 1.87 g of red-purple crystals. Further workup of the filtrate yielded 0.37 g of a third batch for a combined yield of 2.67 g (49% yield). NMR data in C_6D_6 show four signals each of relative intensity 1 at 8.01 (doublet), 6.26 (triplet), 6.12 (doublet), and 5.80 (triplet) ppm. Mass spectroscopic data show a weak parent peak due to ^{184}W(η^2-mp)$_2$(CO)$_3$ at *m/e* = 488 with the characteristic isotope pattern of W: ^{182}W = 26.4%, ^{183}W = 14.4%, ^{184}W = 30.6%, and ^{186}W = 28.4%. Additional *m/e* peaks showing this pattern and based on ^{184}W were assigned the following: W(η^2-mp)$_2$(CO)$_2$ = 460, W(η^2-mp)$_2$(CO) = 432, W(η^2-mp)$_2$ = 404. Peaks assigned to loss of C_5H_4N from the mp ligand are W(η^2-mp)(=S) at 326 and W(=S)$_2$ at 248.

The complex W(η^2-mp)$_2$(CO)$_3$ is also readily obtained by stirring a slurry of W(Py)$_3$(CO)$_3$ and pyridine disulfide in methylene chloride overnight. Trace amounts of the complex W(η^2-mp)$_4$ (see below) are formed in these reactions and give a characteristic purple tint to the normally red-orange solutions of W(η^2-mp)$_2$(CO)$_3$. This side product can be maintained at a low level by use of a slight molar excess of the W starting material. Solid W(η^2-mp)$_2$(CO)$_3$ can be stored and handled in air without noticeable decomposition. Solutions of W(η^2-mp)$_2$(CO)$_3$ are somewhat air-sensitive but show no signs of decomposition or loss of CO when maintained under argon at room temperature in the dark over a period of days.

Preparation of W(η^2-mp)$_4$ from W(Py)$_3$(CO)$_3$ and 2PySSPy. In a glovebox a 500 mL round-bottom flask was filled with 0.65 g of W(Py)$_3$(CO)$_3$ [0.00129 mol] and 0.563 g of PySSPy [0.00255 mol]. Approximately 50 mL of CH_2Cl_2 was added, and the mixture in the stoppered flask was stirred overnight. During this time all solids dissolved, and the solution color changed from clear red to intense purple. An aliquot of heptane was added, and the solution was left standing for a week. Air-stable emerald-green crystals slowly formed and precipitated during this time. These crystals were isolated and washed with a small amount of heptane, yielding 0.33 g (41%). The filtrate was concentrated and stored in the glovebox and later yielded an additional 0.1 g for a combined yield of 53%. Anal. Calcd for W(S−C_5H_4N)$_4$: C = 38.5, H = 2.6, N = 9.0, W = 29.5. Found: C = 38.18, H = 2.72, N = 8.94, W = 28.7. Mass spectroscopic data show a strong parent peak due to ^{184}W(η^2-mp)$_4$ at *m/e* = 624 with the characteristic isotope pattern of W: ^{182}W = 26.4%, ^{183}W = 14.4%, ^{184}W = 30.6%,

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and ^{186}W = 28.4%. Additional *m*/*e* peaks showing this pattern and based on ^{184}W were assigned as follows: W(η^2-mp)$_3$(=S) = 546, W(η^2-mp)$_3$ = 514, W(η^2-mp)$_2$(=S) = 436. NMR data in C_6D_6 show signals at 9.09 (doublet, relative area = 1), 6.24 (multiplet, relative area = 1), and 5.96 (multiplet, relative area = 2) ppm.

Preparation of W(η^2-mp)$_4$ from W(η^2-mp)$_2$(CO)$_3$ and PySSPy. The complex W(η^2-mp)$_4$ is readily prepared by direct reaction of W(η^2-mp)$_2$(CO)$_3$ and PySSPy in either methylene chloride or toluene solution. In a typical reaction a solution of W(η^2-mp)$_2$(CO)$_3$ obtained from reaction of 0.41 g of (CHPT)W(CO)$_3$ as described above was reacted with an additional equivalent of PySSPy over a period of several hours. Workup from methylene chloride/heptane solution produced a final yield of emerald-green crystals of 0.225 g, 41% based on the (CHPT)W(CO)$_3$ starting material. The complex W(η^2-mp)$_4$, which is emerald-green as a solid, dissolves in either CH_2Cl_2 or toluene to give an intensely purple solution. Well-formed crystals obtained by several different techniques and solvent combinations failed to give a set of data that could be resolved to a final structure.

Reaction of (η^2-mp)$_2$W(CO)$_3$ and NO. In a 50 mL Schlenk tube under argon atmosphere a solution of W(η^2-mp)$_2$(CO)$_3$ (0.1 g) was prepared in 20 mL of CH_2Cl_2. This solution was transferred by syringe to a thermostated glass reactor filled with 1 atm of NO. The solution was maintained at 25 °C and monitored by FTIR spectroscopy over a period of several hours. The ν_{CO} bands of W(η^2-mp)$_2$(CO)$_3$ (2022 and 1928 cm^{-1}) smoothly decreased as ν_{NO} bands at 1744 and 1644 cm^{-1} of W(η^2-mp)$_2$(NO)$_2$ increased. The reaction was clean and quantitative in solution as judged by analysis of FTIR data. After several hours of reaction, excess NO was removed by evacuation and the methylene chloride solution was filtered into a clean tube and layered with heptane. Over a period of 10 days, yellow crystals of W(η^2-mp)$_2$(NO)$_2$ suitable for structural analysis were obtained.

Reaction of (η^2-mp)$_2$W(CO)$_3$ and PySSPy/NO. In a 50 mL Schlenk tube under an argon atmosphere a solution containing W(η^2-mp)$_2$(CO)$_3$ (0.1 g) and PySSPy (0.024 g) [W/mp molar ratio 1/1] was prepared in 20 mL of CH_2Cl_2. This solution was transferred by syringe to a thermostated glass reactor filled with 1 atm of NO. The solution was maintained at 25 °C and monitored by FTIR spectroscopy over a period of several hours. The ν_{CO} bands of W(η^2-mp)$_2$(CO)$_3$ (2022 and 1928 cm^{-1}) smoothly decreased as ν_{NO} bands at 1744 and 1644 cm^{-1} of W(η^2-mp)$_2$(NO)$_2$ together with a single ν_{NO} band at 1626 cm $^{-1}$ assigned to W(η^2-mp)$_3$(NO) increased. The solution developed a faint purple color characteristic of W(η^2-mp)$_4$, but quantitative analysis of the FTIR data indicated a product distribution of W(η^2-mp)$_2$(NO)$_2$ $\approx$ 85%, W(η^2-mp)$_3$(NO) $\approx$ 12%, and W(η^2-mp)$_4$ = trace. After several hours excess NO was removed by evacuation and the methylene chloride solution was filtered into a clean tube and layered with heptane. The first crystals to develop were W(η^2-mp)$_3$(NO). Further workup of the filtrate yielded W(η^2-mp)$_2$(NO)$_2$, characterized as described above. Mass spectroscopic data show a weak parent peak due to ^{184}W(η^2-mp)$_3$(NO) at *m*/*e* = 544 with the characteristic isotope pattern of W: ^{182}W = 26.4%, ^{183}W = 14.4%, ^{184}W = 30.6%, and ^{186}W = 28.4%. Additional peaks showing this pattern and based on ^{184}W were assigned as W(η^2-mp)$_3$ = 514 and W(η^2-mp)$_2$(NO) = 434.

Reaction performed in a fashion identical to that described above but with a large excess of PySSPy [W/mp molar ratio 1/10] gave a product distribution as follows: W(η^2-mp)$_2$(NO)$_2$ $\approx$ 73%; W(η^2-mp)$_3$(NO) $\approx$ 26%; W(η^2-mp)$_4$ = trace. Reactions performed in the presence of added PhS−SPh [W/PhS−SPh molar ratio 1/10] showed quantitative formation of W(η^2-mp)$_2$(NO)$_2$, and the solutions remained clear yellow.

X-ray Experiments. Data Collection. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ = 0.710 73 Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) were collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on *I* was less than 1%). Absorption corrections by integration were applied on the basis of measured indexed crystal faces.

The structure was solved by the direct methods in SHELXTL5 and refined using full-matrix least squares.[14] The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms.

a. W(η^2-mp)$_2$(CO)$_3$. Crystals were grown under an argon atmosphere by slow diffusion of heptane into a concentrated methylene chloride solution. Red-brown plates precipitated out and were mounted for diffraction study. A total of 191 parameters were refined in the final cycle of refinement using 2837 reflections with $I > 2\,\sigma(I)$ to yield R1 and wR2 of 2.41% and 5.55%, respectively.

b. W(η^2-mp)$_2$(NO)$_2$. Crystals were grown under an argon atmosphere by slow diffusion of heptane into a concentrated methylene chloride solution. Yellow plates precipitated out and were mounted for diffraction study. The asymmetric unit consists of two complexes that are crystallographically independent but chemically equivalent. A total of 344 parameters were refined in the final cycle of refinement using 3085 reflections with $I > 2\,\sigma(I)$ to yield R1 and wR2 of 2.35% and 6.15%, respectively.

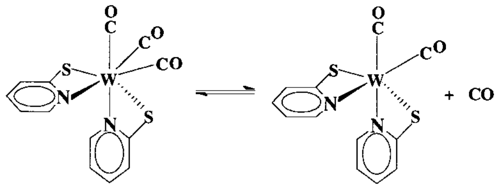
c. W(η^2-mp)$_3$(NO). Crystals were grown under an argon atmosphere by slow diffusion of heptane into a concentrated methylene chloride solution. Yellow-green plates precipitated out and were mounted for diffraction study. The asymmetric unit consists of a half complex (located on a mirror plane at $^1/_4$ in *y*) and a half methylene chloride disordered around a center of inversion. The Cl atoms of each part are related by symmetry; thus, only the CH_2 unit of each disordered part was actually disordered. The methylene chloride was refined in two parts, major and minor. Their site occupation factors were dependently refined to 0.50(1) for each. A total of 162 parameters were refined in the final cycle of refinement using 2238 reflections with $I > 2\,\sigma(I)$ to yield R1 and wR2 of 1.56% and 3.72%, respectively.

Results and Discussion

Synthesis and Structure of W(η^2-mp)$_2$(CO)$_3$. The complex W(η^2-mp)$_2$(CO)$_3$ is readily obtained by oxidative addition reactions such as

$$L_3W(CO)_3 + PyS{-}SPy \rightarrow W(\eta^2\text{-mp})_2(CO)_3 + 3L \quad (7)$$

where L = Py, $^1/_3$CHPT. The 18-electron tricarbonyl complex W(η^2-mp)$_2$(CO)$_3$ is stable and readily isolated. While there is kinetic evidence of loss of CO in some reaction pathways,[15] the equilibrium shown in



(8)

lies far to the left for the chelating system. No spectroscopic evidence can be found to indicate the presence of a stable dicarbonyl complex even after prolonged storing under vacuum at room temperature. That is in stark contrast to W(SPh)$_2$(phen)(CO)$_2$, which is formed immediately upon release of CO pressure from solutions of W(SPh)$_2$(phen)(CO)$_3$, as shown in eq 2. The complexes W(SPh)$_2$(phen)(CO)$_3$ and W(η^2-mp)$_2$(CO)$_3$ are both W(II) containing similar ligand sets [two arene thiolate ligands, two aromatic nitrogen donors, and three CO ligands]. More facile dissociation of W(SPh)$_2$(phen)(CO)$_3$ may be due to the fact that loss of CO yields W(SPh)$_2$(phen)(CO)$_2$, which adopts a nearly pure octahedral geometry together. Loss of CO from W(η^2-mp)$_2$(CO)$_3$ yielding W(η^2-mp)$_2$(CO)$_2$ may not allow the same degree of rearrangement because the acute “bite” of the mp ligand prevents expansion to a wider angle. Regardless

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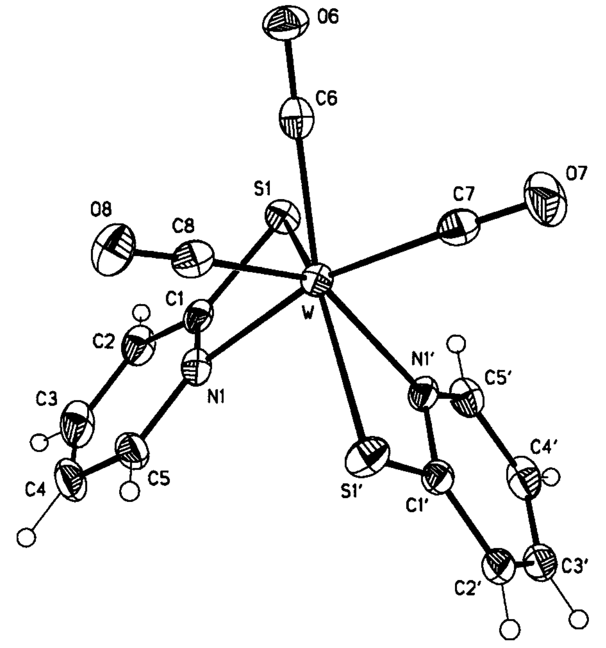


Figure 1. Ortep drawing of W(η^2-mp)$_2$(CO)$_3$.

Table 1. Crystallographic Data and Structure Refinement for W(η^2-mp)$_2$(CO)$_3$, W(η^2-mp)$_2$(NO)$_2$, and W(η^2-mp)$_3$(NO)

space group	*P*2(1)/*c*	$P\bar{1}$	*Pnma*
a, Å	11.8939(7)	8.2604(3)	15.0210(6)
b, Å	9.4778(5)	12.6162(5)	15.0846(6)
c, Å	13.3415(8)	12.7995(5)	8.9312(4)
α, deg	90	91.720(1)	90
β, deg	100.391(1)	95.989(1)	90
γ, deg	90	92.242(1)	90
V, Å^3	1479.3(2)	1324.82(9)	2023.7(1)
fe	488.18	464.17	629.24
ρ_{calcd}, Mg/m^3	2.192	2.327	2.065
chem formula	$C_{13}H_8N_2O_3S_2W$	$C_{10}H_8N_4O_2S_2W$	$C_{16}H_{14}Cl_2N_4OS_3W$
Z	4	4	4
μ, mm^{-1}	8.100	9.036	6.297
T, °C	−100	−100	−100
λ, Å	0.710 73	0.710 73	0.710 73
R1 [a]	0.0241	0.0235	0.0156
wR2 [b] [$I > 2\sigma(I)$]	0.0555 [2837]	0.0615 [5456]	0.0372 [2238]

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ [$I > 2\sigma(I)$].

of the reason, the W−CO bond in W(η^2-mp)$_2$(CO)$_3$ is observed to be significantly stronger than in W(SPh)$_2$(phen)(CO)$_3$, where $D_{W-CO} \approx 7$ kcal/mol.[3]

The crystal structure of the seven-coordinate W(II) bisthiolate is shown in Figure 1, and selected data are shown in Tables 1 and 2. Full data are available as Supporting Information. The crystal structure bears a strong resemblance to that of the related pyrimidine analogue W(η^2-mpd)$_2$(CO)$_3$, described as a capped trigonal prism by Baker[7] and co-workers. There are several idealized geometries that seven-coordinate complexes can display,[16] and in practice it can be difficult to determine which of the ideal structures is closest to the actual one. For example, the similar complex W(η^2-mp)2(CO)$_2$(PMe$_2$Ph) was described by Deeming[6] as being close to both the capped octahedral and 4:3 piano-stool geometries.

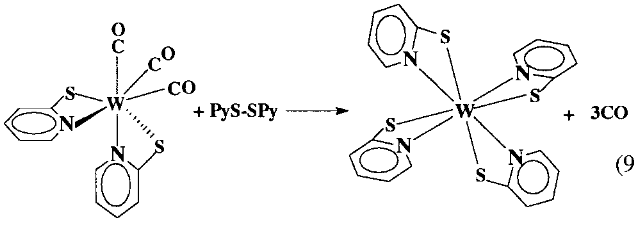
The coordinatively saturated complex W(η^2-mp)$_2$(CO)$_3$ has longer W−S bond vectors [2.5067(10) and 2.5330(11) Å] than does the formally 16-electron complex W(SPh)$_2$(CO)$_2$(phen) [2.354(2) and 2.368(2) Å]. However, the W−N distances have nearly identical average values: [2.201(3) and 2.231(3) Å for W(η^2-mp)$_2$(CO)$_3$ compared to values of 2.217(5) and 2.215 Å for W(SPh)$_2$(CO)$_2$(phen).[3] This may imply that the burden of the strain in the four-membered chelate ring [W−S−N angles of 64.83(9)° and 64.99(9)°] is placed on the W−S bond rather than on the W−N bond. However, it should be pointed out that the shorter W−S distances in the formally 16-electron complex W(SPh)$_2$(phen)(CO)$_2$ may also be a consequence of partial multiple bond character involving additional donation from sulfur to W in this complex to compensate for loss of the seventh ligand. None of the structures reported show distortion of the planarity of the pyridine ring system.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for W(η^2-mp)$_2$(CO)$_3$[a]

W−S1	2.5067(10)	W−C8	1.994(4)
W−S1′	2.5330(11)	C6−O6	1.147(5)
W−N1	2.201(3)	C7−O7	1.137(5)
W−N1′	2.231(3)	C8−O8	1.135(5)
W−C6	1.989(5)	S1−C1	1.737(4)
W−C7	2.009(5)	S1′−C1′	1.745(4)
C6−W−C8	73.78(17)	C7−W−S1′	79.37(14)
C6−W−C7	75.48(17)	N1−W−S1′	91.36(10)
C8−W−C7	104.98(18)	N1′−W−S1′	64.99(9)
C6−W−N1	117.77(15)	S1−W−S1′	144.06(4)
C8−W−N1	84.38(15)	C1−S1−W	81.72(14)
C7−W−N1	165.92(16)	C5−N1−W	135.8(3)
C6−W−N1′	139.67(15)	C1−N1−W	103.5(3)
C8−W−N1′	146.02(15)	N1−C1−S1	109.9(3)
C7−W−N1′	84.05(16)	C2−C1−S1	129.1(4)
N1−W−N1′	82.42(12)	C1′−S1′−W	81.02(15)
C6−W−S1	75.21(11)	C5′−N1′−W	137.8(3)
C8−W−S1	117.39(12)	C1′−N1′−W	102.3(3)
C7−W−S1	117.69(13)	N1′−C1′−S1′	111.7(3)
N1−W−S1	64.83(9)	C2′−C1′−S1′	127.1(4)
N1′−W−S1	84.57(9)	O6−C6−W	178.6(4)
C6−W−S1′	140.61(12)	O7−C7−W	177.7(4)
C8−W−S1′	84.23(12)	O8−C8−W	176.7(4)

[a] Full data are available as Supporting Information.

Reaction of W(η^2-mp)$_2$(CO)$_3$ and PyS−SPy To Form W(η^2-mp)$_4$. In the presence of excess additional pyridine disulfide, solutions of W(η^2-mp)$_2$(CO)$_3$ were found to slowly turn from red-orange to purple. The resulting complex W(η^2-mp)$_4$, which can be isolated as a beautiful emerald-green crystalline solid, is formed according to



(9)

Direct preparation of this complex is also readily accomplished by reaction of L$_3$W(CO)$_3$ [L = Py, 1/3 CHPT] with 2 equiv of disulfide:

$$L_3W(CO)_3 + 2PyS{-}SPy \rightarrow W(\eta^2\text{-mp})_4 + 3L + 3CO \quad (10)$$

Elemental analysis [C, H, N, W], ^{1}H NMR, and mass spectroscopy were used to characterize the complex. Several attempts to determine the crystal structure of W(η^2-mp)$_4$ were not successful. Crystals of W(η^2-mp)$_4$ are severely twinned. Several approximate solutions, but from huge lattice unit cells, could be obtained and were supportive of an eight-coordinate mono-

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(16) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M.; *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 7. (b) Lippard, S. J. *Prog. Inorg. Chem.* **1976**, *21*, 91.

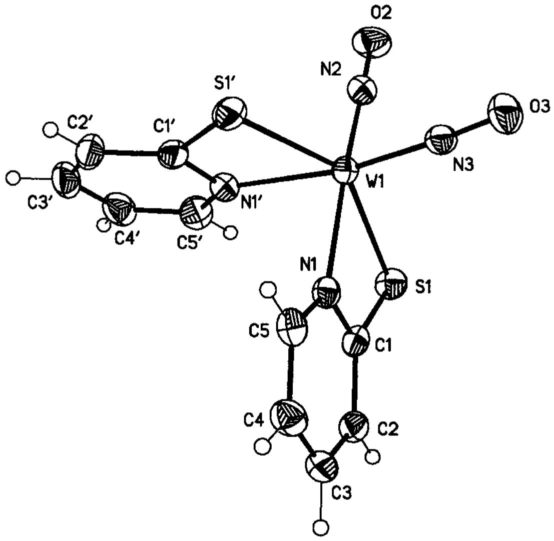
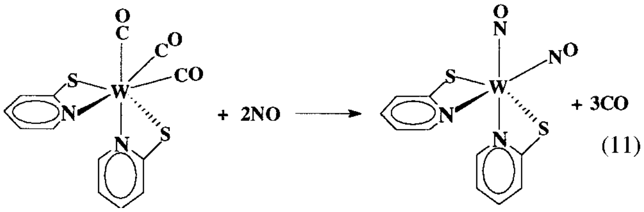


Figure 2. Ortep drawing of W(η^2-mp)$_2$(NO)$_2$.

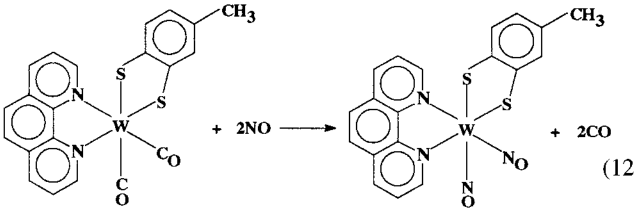
mer. However, the data obtained were not of high enough quality for publication. Attempts are in progress to improve the crystal quality, solution, and refinement. The analytical data unequivocally support the formulation as W(η^2-mp)$_4$, and the solubility and presence of a strong parent peak in the mass spectroscopic data all support its formulation as a monomer. In view of the literature structures[8,9] of M(η^2-mpd)$_4$ [M = Mo, W], W(η^2-mp)$_4$ is formulated as an eight-coordinate monomeric W(IV) complex.

Reaction of W(η^2-mp)$_2$(CO)$_3$ with NO To Yield W(η^2-mp)$_2$(NO)$_2$. Reaction of pure samples of W(η^2-mp)$_2$(CO)$_3$ give quantitative formation of the bisnitrosyl product as shown:



(11)

The bis-nitrosyl product is formed with no sign of formation of nitrosylthiol, as shown for W(SPh)$_2$(phen)(CO)$_2$ in eq 3. In this regard, the reaction with nitric oxide resembles that observed earlier[4] for W(phen)(η^2-S,S−arene)(CO)$_2$, which proceeds by elimination of CO:



(12)

Apparently, having the sulfur atom as part of a chelate ring system reduces the tendency for nitrosothiol reductive elimination for the complexes in eqs 11 and 12 when compared to the analogous reaction in eq 3. In addition, the rate of reaction 11 is much slower than the rates of reactions 3 and 12, as would be expected for the reactivity of the formally 18- versus 16-electron complexes.

The crystal structure of W(η^2-mp)$_2$(NO)$_2$ is shown in Figure 2, with selected data in Tables 1 and 3. The distorted octahedral structure apparent in this drawing has the two NO ligands roughly trans to the nitrogen atoms of the coordinating pyridines and nearly orthogonal to each other [ON−W−NO = 89.83(14)°]. In this regard it resembles the previously reported octahedral structure for W(phen)(η^2-S,S−toluene)(NO)$_2$ which has an ON−W−NO angle of 88.8(2)°. The W−S bond lengths in W(η^2-mp)$_2$(NO)$_2$ [2.4695(10) and 2.4760(9) Å] are shorter than those in W(η^2-mp)$_2$(CO)$_3$ [2.5330 and 2.5067 Å as discussed above] and somewhat longer than those in W(phen)(η^2-S,S−toluene)(NO)$_2$ [2.423(1) and 2.461(1) Å]. As structural and calorimetric data are extended for a range of analogous complexes, more detailed analysis of these metrical parameters may be warranted.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for W(η^2-mp)$_2$(NO)$_2$[a]

W1−N2	1.827(3)	W2−N13	1.827(3)
W1−N3	1.828(3)	W2−N12	1.835(3)
W1−N1′	2.198(3)	W2−N11	2.196(3)
W1−N1	2.210(3)	W2−N11′	2.199(3)
W1−S1′	2.4695(10)	W2−S11′	2.4830(10)
W1−S1	2.4760(9)	W2−S11	2.4872(10)
S1−C1	1.748(4)	S11−C11	1.750(4)
S1′−C1′	1.748(4)	S11′−C11′	1.739(4)
N2−O2	1.183(4)	N12−O12	1.179(4)
N3−O3	1.184(4)	N13−O13	1.189(4)
O2−N2−W1	178.1(3)	N1′−W1−S1	89.44(9)
O3−N3−W1	176.1(3)	N1−W1−S1	65.88(8)
N2−W1−N3	89.83(14)	S1′−W1−S1	145.53(3)
N2−W1−N1′	90.06(13)	C1−S1−W1	81.53(12)
N3−W1−N1′	167.63(13)	C5−N1−W1	137.9(3)
N2−W1−N1	167.07(13)	C1−N1−W1	101.8(2)
N3−W1−N1	96.49(13)	N1−C1−S1	110.8(3)
N1′−W1−N1	86.16(11)	C2−C1−S1	127.6(3)
N2−W1−S1′	102.62(11)	C1′−S1′−W1	81.40(13)
N3−W1−S1′	101.38(10)	C5′−N1′−W1	138.4(3)
N1′−W1−S1′	66.61(9)	C1′−N1′−W1	101.1(3)
N1−W1−S1′	87.22(8)	N1′−C1′−S1′	110.8(3)
N2−W1−S1	101.76(11)	C2′−C1′−S1′	128.5(3)
N3−W1−S1	102.69(10)		

[a] Full data are available as Supporting Information.

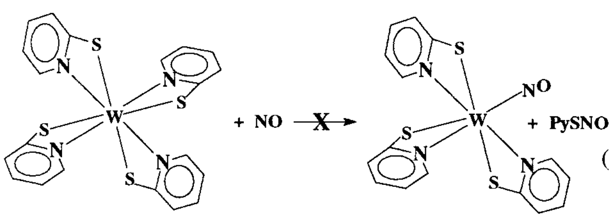
Reaction of W(η^2-mp)$_2$(CO)$_3$ with NO in the Presence of PyS−SPy To Yield W(η^2-mp)$_3$(NO). Reaction of W(η^2-mp)$_2$(CO)$_3$ with NO in the presence of additional excess pyridine disulfide proceeds as shown:

$$\begin{array}{l} \mathrm{W}(\eta^2\text{-mp})_2(\mathrm{CO})_3 + \mathrm{PySSPy} \xrightarrow{\mathrm{NO}} \\ \qquad \underset{\text{trace}}{\mathrm{W}(\eta^2\text{-mp})_4} + \underset{75-85\%}{\mathrm{W}(\eta^2\text{-mp})_2(\mathrm{NO})_2} + \underset{10-25\%}{\mathrm{W}(\eta^2\text{-mp})_3(\mathrm{NO})} \end{array} \quad (13)$$

In the presence of 1 atm of NO, only trace amounts of W(η^2-mp)$_4$ are formed. The two dominant products are W(η^2-mp)$_2$(NO)$_2$ and W(η^2-mp)$_3$(NO). The exact ratio of products depends on the PySSPy/NO/W ratio, and the kinetics and mechanism of this reaction are under detailed investigation. Because of its lower solubility, crystalline W(η^2-mp)$_3$(NO) may crystallize preferentially despite being present as a minor product.

The complex W(η^2-mp)$_3$(NO) was discovered accidentally during an attempt to prepare a sample of W(η^2-mp)$_2$(NO)$_2$ according to eq 12 to grow crystals for structural analysis. A crude solution of W(η^2-mp)$_2$(CO)$_3$ obtained from an in situ reaction must have contained unreacted PySSPy. The yellow-green crystals first selected for structural analysis did not prove to be the expected six-coordinate W(η^2-mp)$_2$(NO)$_2$ (Figure 2) but the seven-coordinate complex W(η^2-mp)$_3$(NO) as shown in Figure 3 [this structure was actually determined prior to that of the expected product W(η^2-mp)$_2$(NO)$_2$].

Initially it was believed that W(η^2-mp)$_3$(NO) might have been obtained from reaction of W(η^2-mp)$_4$ and NO:

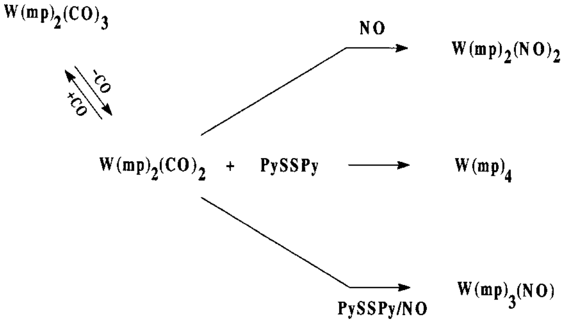


(14)

However, under 1 atm of NO at room temperature, reaction 14 does not occur. A second possibility was that W(η^2-mp)$_2$(NO)$_2$ is formed first and is slowly converted to W(η^2-mp)$_3$(NO) in the presence of W(η^2-mp)$_4$ or PySSPy—the two most likely contaminants of the crude sample of W(η^2-mp)$_2$(CO)$_3$ used in the first experiment. Neither of these reactions generate detectable amounts of W(η^2-mp)$_3$(NO).

Studies show that W(η^2-mp)$_3$(NO) is produced continuously during the reaction and that the presence of both NO and PySSPy is required for its formation. The coordinating ability through its nitrogen donor atoms may play a role in the formation of W(η^2-mp)$_3$(NO) in reaction 13. Reaction with PhS−SPh/NO in a manner analogous to that shown in reaction 13 produced only W(η^2-mp)$_2$(NO)$_2$ and did not show signs of formation of either W(η^2-mp)$_2$(SPh)(NO) or W(η^2-mp)$_2$(SPh)$_2$, that is, the products corresponding to W(η^2-mp)$_3$(NO) or W(η^2-mp)$_4$, respectively. In addition, deliberate injection of oxygen does not lead to production of W(η^2-mp)$_3$(NO), implying that W(η^2-mp)$_3$(NO) is not produced from reactions involving radical attack by NO$_2$. No sign of formation of N$_2$O was observed during these reactions.

These observations support the following tentative mechanism:



(15)

Reaction 15 proposes reversible generation of the 16-electron complex W(η^2-mp)$_2$(CO)$_2$ [analogous to W(SPh)(phen)(CO)$_2$ in eq 2]. This intermediate can be trapped by NO to yield W(η^2-mp)$_2$(NO)$_2$ as shown in the top line, can coordinate and then undergo oxidative addition with an additional mole of PySSPy to yield W(η^2-mp)$_4$ as shown in the middle line, or can coordinate PySSPy and have this intermediate intercepted by NO to yield W(η^2-mp)$_3$(NO) as shown in the bottom line. The failure of PhSSPh to enter into this reaction scheme may be due to the weaker donor ability of the S atom of a coordinating disulfide ligand when compared to the N donor in pyridine disulfide. *Coordination of pyridine disulfide through the nitrogen atom may thus serve to activate it toward oxidative addition at the metal center in the presence of NO.*

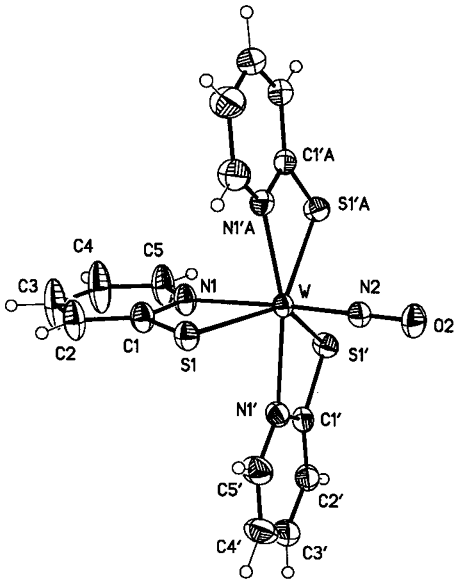


Figure 3. Ortep drawing of W(η^2-mp)$_3$(NO).

Table 4. Selected Bond Lengths [Å] and Angles [deg] for W(η^2-mp)$_3$(NO)[a]

W−N2	1.779(3)	W−S1′	2.5204(6)
W−N1	2.215(3)	W−S1′A	2.5204(6)
W−N1′	2.220(2)	S1−C1	1.753(4)
W−N1′A	2.220(2)	S1′−C1′	1.733(2)
W−S1	2.4853(8)	O2−N2	1.215(4)
O2−N2−W	179.8(3)	N2−W−S1′A	97.89(7)
N2−W−N1	171.30(11)	N1−W−S1′A	89.15(6)
N2−W−N1′	91.77(5)	N1′−W−S1′A	135.11(5)
N1−W−N1′	86.76(5)	N1′A-W−S1′A	63.73(5)
N2−W−N1′A	91.77(5)	S1−W−S1′A	137.240(17)
N1−W−N1′A	86.76(5)	S1′−W−S1′A	71.53(3)
N1′−W−N1′A	159.92(10)	C1−S1−W	81.62(11)
N2−W−S1	105.46(9)	C5−N1−W	137.5(2)
N1−W−S1	65.85(7)	C1−N1−W	101.9(2)
N1′−W−S1	80.00(5)	N1−C1−S1	110.6(2)
N1′A-W−S1	80.00(5)	C2−C1−S1	128.1(3)
N2−W−S1′	97.89(7)	C1′−S1′−W	82.87(8)
N1−W−S1′	89.15(6)	C5′−N1′−W	136.32(17)
N1′−W−S1′	63.73(5)	C1′−N1′−W	104.69(15)
N1′A-W−S1′	135.11(5)	N1′−C1′−C2′	122.0(2)
S1−W−S1′	137.240(16)	C2′−C1′−S1′	129.3(2)

[a] Full data are available as Supporting Information.

The structure of W(η^2-mp)$_3$(NO) is approximately a pentagonal bipyramid as shown in Figure 3. Data for this structure are listed in Tables 1 and 4. The NO ligand is roughly trans to one of the coordinating pyridines (N1−W−N2 = 171.3°), and the remaining five donor atoms are approximately planar with S1 pulled below the plane by 0.88 Å because of steric factors from the ligand. As discussed earlier, it can be difficult to classify seven-coordinate structures such as W(η^2-mp)$_2$(CO)$_3$ (Figure 1) and W(η^2-mp)$_3$(NO) (Figure 3), which do not exactly match any of the idealized geometries. Nevertheless, there are significant differences between these two structures. The NO ligand, despite its small size, forces the thiopyridines away from it with all angles to it greater or equal to 90°: N2−W−N1′A = 91.77°, N2−W−S1′A 97.89°, N2−W−S1′ = 97.89°, N2−W−N1′ = 91.77°, and N2−W−S1 = 105.46°. The strong π-bonding character of the W−NO bond may be responsible for the fact that the three chelating ligands are at or below an equatorial position in the structure.

The geometry around the metal center and the M−N−O angles in both W(η^2-mp)$_2$(NO)$_2$ and W(η^2-mp)$_3$(NO) classify them as linear nitrosyls[17] and hence NO$^+$ derivatives. Data for the W(N-donor)$_2$(SR)$_x$(CO)$_y$(NO)$_z$ prepared by us to date are summarized in Table 5. The shortest W−NO bond occurs for the seven-coordinate W(II) structure in W(η^2-mp)$_3$(NO). In

Table 5: Comparison of Selected Structural Data for NO Complexes

complex	W−N−O angle (deg)	ON−W−NO angle (deg)	W−NO length (Å)	N−O length (Å)	ν_{NO} (cm^{-1}) (CH_2Cl_2 solution)
W(phen)(SPh)$(CO)_2$(NO), octahedral W(0)[a]	176.6	NA	1.825	1.199	1608
W(phen)(S,S−toluene)$(NO)_2$, octahedral W(0)[a]	175.7	88.8	1.815[c]	1.197[c]	1721,1630
	175.5		1.835[d]	1.180[d]	(toluene)
W(η^2-mp)$_2$$(NO)_2$,[b] distorted octahedral W(0)	178.3	89.8	1.827	1.183	1744,1644
	177.5		1.828	1.184	
W(η^2-mp)$_3$(NO),[b] distorted pentagonal bipyramid W(II)	179.8	NA	1.779	1.215	1626

[a] Data taken from ref 3. [b] This work. [c] For NO ligand trans to N donor atom of Phen ligand. [d] For NO ligand trans to S donor atom of (S,S−toluene) ligand.

addition, the N−O bond length is longest for this complex, which is consistent with more significant back-bonding in this system. It should be noted, however, that there is no clear-cut correlation between ν_{NO} and d_{N-O} in the data in Table 5.

An additional point of interest is comparison of the two complexes W(η^2-mp)$_2$$(NO)_2$ and W(phen)(η^2-S,S-Toluene)-$(NO)_2$, both of which are essentially octahedral in their geometry with two cis NO ligands, two arene thiolates, and two aromatic N donors. One major difference between these complexes is the possible role of steric strain in the two four-membered rings in W(η^2-mp)$_2$$(NO)_2$ as opposed to the two five-membered rings present in W(phen)(η^2-S,S−toluene)$(NO)_2$. The second geometric difference arises from the presence of two equivalent chelating S,N donors in W(η^2-mp)$_2$$(NO)_2$ as opposed to two N,N and S,S donors in W(phen)(η^2-S,S−toluene)$(NO)_2$. This has the consequence that while both NO's are positioned trans to pyridine donors in W(η^2-mp)$_2$$(NO)_2$, for W(phen)($\eta^2$-S,S−toluene)$(NO)_2$ only one NO is trans to a pyridine donor; the other is forced to occupy a position trans to a sulfur donor. As shown in Table 5, the values for ν_{NO} are lower for W(phen)-(η^2-S,S−toluene)$(NO)_2$, as is the W−NO distance for NO trans to the phenanthroline donor. For this complex, the N−O bond distance is longer as well, in keeping with more significant donation from W to NO for this NO. As might be expected, the situation is reversed for the NO in W(phen)(η^2-S,S−toluene)$(NO)_2$, which is trans to the sulfur atom. It will be of interest to determine experimentally if differences in enthalpies of formation of these two structurally similar complexes exist and if they can be calculated using theoretical techniques.

Conclusion

This paper reports our initial studies of reaction of low-valent tungsten carbonyl complexes with pyridine disulfide. A possible consequence of this ligand's relatively small size and "bite" is that higher coordination numbers may be favored. This may explain the stability of the coordinatively saturated seven-coordinate complex W(η^2-mp)$_2$$(CO)_3$, in contrast to W$(SPh)_2$-(phen)$(CO)_3$ and W(η^2-S,S−arene)(phen)$(CO)_3$, both of which readily lose CO to form stable six-coordinate dicarbonyl complexes. Further oxidative addition of W(η^2-mp)$_2$$(CO)_3$ yields W(η^2-mp)$_4$, which is proposed to be eight-coordinate based on its spectroscopic properties. Reaction of W(η^2-mp)$_2$$(CO)_3$ with NO yielded the six-coordinate complex W(η^2-mp)$_2$$(NO)_2$, but in the presence of PySSPy and NO, the reaction yielded in addition the seven-coordinate product W(η^2-mp)$_3$(NO). Attack by NO on coordinated pyridine disulfide appears to be the most likely source of this product.

Acknowledgment. Support of this work by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged (C.D.H.) as well as support by the National Science Foundation and the University of Florida for funding of the purchase of the X-ray equipment (K.A.A.).

Supporting Information Available: X-ray crystallographic files in CIF format for the complexes W(η^2-mp)$_2$$(CO)_3$, W($\eta^2$-mp)$_2$$(NO)_2$, and W($\eta^2$-mp)$_3$(NO). This material is available free of charge via the Internet at http://pubs.acs.org.

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