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Dicarbonyltungsten(II) Thiolate Complexes of Hydridotris(3,5-dimethylpyrazolyl)borate

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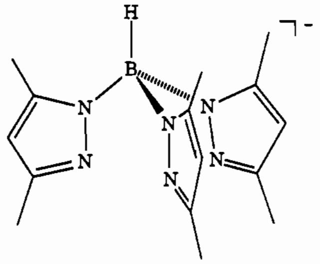
A series of hydridotris(3,5-dimethylpyrazolyl)borate tungsten(II) thiolate complexes of the general type $Tp'W(CO)_2(SR)$ (R = Me, Et, ^iPr, CH_2Ph, and p-$C_6H_4NO_2$) has been synthesized by reaction of the appropriate sodium thiolate or mercaptan with $Tp'W(CO)_2I$ (**1**). The structures of these organothiolate complexes were elucidated on the basis of their IR and ^1H and ^{13}C NMR spectra and elemental analysis data. In addition, single-crystal X-ray diffraction was used to structurally characterize two of the complexes, $Tp'W(CO)_2(S\text{-}p\text{-}C_6H_4NO_2)$ (**4**) and $Tp'W(CO)_2(SCH_2Ph)$ (**7**). Both complexes crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$. Unit cell dimensions for **4** were $a = 10.517(2)$ Å, $b = 12.016(5)$ Å, and $c = 13.904(3)$ Å with angles $\alpha = 77.25(3)°$, $\beta = 76.44(2)°$, and $\gamma = 64.23(2)°$. Refinement of 357 variables over 3706 reflections led to an R value of 0.044 and R_w of 0.065. Unit cell dimensions for **7** were $a = 9.709(2)$ Å, $b = 10.230(2)$ Å, and $c = 15.355(3)$ Å with angles $\alpha = 72.92(2)°$, $\beta = 84.32(2)°$, and $\gamma = 64.87(1)°$. Refinement of 316 variables over 4185 reflections led to an R value of 0.047 and R_w of 0.057. The thiolate substituent is located approximately in the molecular mirror plane in both of these complexes. In each case the OC–W–CO angle is acute for electronic reasons originating in the d^4 metal configuration.

Introduction

The catalytic[2] and biochemical[3] importance of complexes containing thiolate ligands has been well documented. One of the powerful driving forces for pursuing thiolate chemistry has been the quest for a model of the catalytic site of nitrogenase,[4] and hence an extensive literature of molybdenum and other group VI thiolate chemistry has been developed.[5–7] Although low oxidation state group VI carbonyl thiolate chemistry is less mature, molybdenum, tungsten, and chromium cyclopentadienyl complexes containing an alkylthio ligand have been known for approximately 30 years.[8]

The rich chemistry of $[CpCr(CO)_3]_2$ and $[CpMo(CO)_3]_2$[9,10] has led to a variety of thiolate complexes.[11] Reaction of $[CpMo(CO)_3]_2$ with RSSR under UV irradiation gave the $[CpMo(CO)_2(SR)]_2$ dimer.[12,13] Reaction of the $[CpMo(CO)_2]_2$[14] metal–metal triple bond or $CpMo(CO)_3H$[12] with MeSSMe also produced a dimer with the composition $[CpMo(CO)_2(SMe)]_2$. Cyclopentadienylmercaptochromium dimers of different compositions were formed from reactions of $[CpCr(CO)_3]_2$ or $[CpCr(CO)_2]_2$ with Ph_2S_2 at different temperatures.[15]

Hydridotris(pyrazolyl)borato (**I**) molybdenum complexes containing an arylthio ligand were synthesized in low yields by Trofimenko in 1971 by the reaction of $Tp'W(CO)_3^-$ with arenesulfonyl chlorides.[16] These complexes have a stoichiometry and electron count reminiscent of the $[CpM(CO)_2(SR)]_2$ dimers, but they exist as monomers.



Tp' = hydridotris(3,5-dimethylpyrazolyl)borate

I

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In this paper we expand the series of complexes of the general formula Tp′W(CO)$_2$(SR). These complexes serve as a vehicle to present the effects that π-donor ligands have on the electronic structures of complexes containing both π-acid and π-base ligands. The thiolate complexes provide a nice example of simple monomers which count 16-electrons at the metal unless π-donation is considered. The reactivity patterns and spectral properties of these complexes indicate that thiolate π-donation is an important bonding feature here.

Experimental Section

General Procedure and Materials. All reactions were carried out under an atmosphere of dried dinitrogen using standard Schlenk techniques. The ^{1}H and ^{13}C NMR spectra were obtained on a Varian XL-400 spectrometer. Infrared spectra were obtained on a Mattson Polaris FTIR spectrophotometer. Tetrahydrofuran (THF), diethyl ether (Et$_2$O), and hexane were distilled from potassium benzophenone ketyl. Methylene chloride (CH$_2$Cl$_2$) was distilled from P$_2$O$_5$. Methanol (MeOH) and toluene were obtained from Fisher Scientific and used as received. Tp′W(CO)$_3$I[17] was prepared as previously reported. Sodium methanethiolate (NaSMe), sodium ethanethiolate (NaSEt), benzenethiol (PhSH), 2-propanethiol (^{i}PrSH), phenylmethanethiol (PhCH$_2$SH), and *p*-nitrobenzenethiol (*p*-NO$_2$C$_6$H$_4$SH) were obtained from Aldrich and used without further purification.

Preparation of Tp′W(CO)$_2$I (1). In a representative preparation Tp′W(CO)$_3$I (2.00 g, 2.89 mmol) was dissolved in THF (60 mL) and refluxed for 20 h. The product was precipitated from solution by reducing the solvent volume to about 20 mL under vacuum and then cooling the reaction flask in the freezer overnight. The orange-brown, paramagnetic, crystalline material was isolated by filtration of the THF solution and was used as a reagent without further purification. The complex must be stored under N$_2$ because it reacts readily with moist air to produce Tp′WO(CO)I.[18] IR: (THF) ν_{CO} (cm^{-1}) 1944, 1846.

Preparation of Tp′W(CO)$_2$(SMe) (2). In a typical preparation, Tp′W(CO)$_2$I (1.30 g, 1.96 mmol) was dissolved in CH$_2$Cl$_2$ (25 mL) and filtered into a flask containing NaSMe (0.15 g, 2.14 mmol). The reaction mixture was stirred for 15 min and then filtered onto a column of alumina and eluted with CH$_2$Cl$_2$. Evaporation of the orange fraction under vacuum afforded a brown powder. Recrystallization of the powder from a solvent mixture of CH$_2$Cl$_2$/hexane yielded yellow needles when cooled overnight in a −30 °C freezer. Recrystallization of the needles via slow diffusion of either hexane or methanol into a CH$_2$Cl$_2$ solution produced needles as well as blocks of orange crystals which were satisfactory for elemental analysis. Yield, 82%. IR (KBr): ν_{CO} 1930, 1813 cm^{-1}. IR (THF): ν_{CO} 1935, 1823 cm^{-1}. ^{1}H NMR: (CD$_2$Cl$_2$): δ (ppm) 1.73, 2.64 (s, each 6H, Tp′CH_3); 2.04, 2.41 (s, 3:6 H, Tp′CH_3 and SCH_3); 5.91, 6.10 (s, 2:1 H, Tp′*H*). ^{13}C NMR: δ (ppm) 12.6, 13.2, 17.1, 17.5 (2:1:1:2 Tp′*C*H$_3$); 56.0 (S*C*H$_3$); 106.7, 109.8 (2:1 Tp′*C*H); 145.5, 149.1, 150.8, 162.7 (2:1:2:1 Tp′-*C*Me); 252.2 ($^1J_{W-C}$ = 165 Hz, *C*O). Anal. Calcd for C$_{18}$H$_{25}$BN$_6$O$_2$SW: C, 37.01; H, 4.31; N, 14.38. Found: C, 37.22; H, 4.34; N, 14.19.

Preparation of Tp′W(CO)$_2$(SEt) (3). To a solution of 90% pure NaSEt (0.07 g, 0.83 mmol) in 25 mL of CH$_2$Cl$_2$ was added Tp′W(CO)$_2$I (0.45 g, 0.68 mmol). The solution was stirred for 15 min. After the solvent was evaporated in vacuo, the product was redissolved in THF and filtered onto a column of alumina. The pure product was eluted with THF, and the product was isolated as a brown crystalline solid by removing solvent under vacuum. About 100 mg of the powder was dissolved in 2 mL of CH$_2$Cl$_2$ and recrystallized by slow diffusion of the solution into methanol. Filtration of the red solution afforded an analytically pure yellow crystalline solid. Yield: 53%. IR (KBr): ν_{CO} 1927, 1811 cm^{-1}. IR (THF): ν_{CO} 1935, 1823. ^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) 1.46 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, SCH$_2$CH_3); 1.74 (m, 8H, 2Tp′CH_3 and SCH_2CH$_3$); 2.39, 2.40, 2.62 (s, 3:3:6 H, Tp′CH_3); 5.89, 6.08 (s, 2:1 H, Tp′*H*). ^{13}C NMR: (CD$_2$Cl$_2$): δ (ppm) 12.6, 13.2, 16.3, 17.2, 17.7 (2:1:1:1:2 Tp′*C*H$_3$ and SCH$_2$*C*H$_3$); 65.7 (S*C*H$_2$); 106.6, 109.7, (2:1 Tp′-*C*H); 145.5, 149.0, 151.9, 162.7 (2:1:2:1 Tp′*C*H$_3$); 252.2 ($^1J_{W-C}$ = 166 Hz, *C*O). Anal. Calcd for C$_{19}$H$_{27}$BN$_6$O$_2$SW·$^1/_2$CH$_2$Cl$_2$: C, 36.55, H, 4.40; N, 13.12. Found: C, 36.52; H, 4.54; N, 12.80.

Preparation of Tp′W(CO)$_2$(S-*p*-C$_6$H$_4$NO$_2$) (4). To a solution of excess 80% pure HS(*p*-C$_6$H$_4$NO$_2$) in THF (25 mL) was added Tp′W(CO)$_2$I (0.46 g, 0.70 mmol). The reaction was stirred for 10 min. After reduction of solvent volume to about 10 mL, the solution was loaded onto a column of alumina and eluted with THF. The product was isolated by solvent removal under vacuum, and then the solid was rinsed with methanol. Recrystallization of the product by slow diffusion of a CH$_2$Cl$_2$ solution into methanol afforded red, analytically pure crystals. Yield: 65%. IR (KBr): ν_{CO} (cm^{-1}) 1939, 1829 (br). IR (THF): ν_{CO} (cm^{-1}) 1942, 1834. ^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) 1.43, 2.34, 2.39, 2.66 (s, 6:3:3:6 H, Tp′CH_3); 5.70, 6.09 (s, 2:1 H, Tp′*H*); 6.81, 6.84 (d, $^3J_{H-H}$ = 9 Hz, each 2H, AA′BB′ aromatic-*H*). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 12.5, 13.2, 17.2, 17.4 (2:1:2:1 Tp′*C*H$_3$); 106.9, 110.2 (2:1 Tp′*C*H); 124.3, 129.6, (phenyl-*C*); 146.3, 146.4, 150.3, 151.5, 164.1, 179.9 (2:1:1:2:1:1Tp′*C*-CH$_3$, phenyl-*C*NO$_2$ and phenyl-*C*S); 247.2 ($^1J_{W-C}$ = 161 Hz, CO). Anal. Calcd for C$_{23}$H$_{26}$BN$_7$O$_4$SW·$^1/_2$ CH$_2$Cl$_2$: C, 39.37; H, 3.79; N, 13.66. Found: C, 39.10; H, 4.00; N, 13.26.

Preparation of Tp′W(CO)$_2$(SPh) (5). To a THF solution (25 mL) of Tp′W(CO)$_2$I (662 mg, 1.00 mmol) was added a slight excess of PhSH. The solution was stirred overnight. The solution volume was reduced in vacuo to about 10 mL, and the product was purified by column chromatography using CH$_2$Cl$_2$ as the eluent with an alumina column. The CH$_2$Cl$_2$ solution was then evaporated and the resultant solid was recrystallized from CH$_2$Cl$_2$/hexanes or CH$_2$Cl$_2$/MeOH to form an analytically pure crystalline solid. Yield: 71%. IR (KBr): ν_{CO} (cm^{-1}) 1933, 1923, 1819, 1805. IR (THF): ν_{CO} (cm^{-1}) 1937, 1827. ^{1}H NMR (CDCl$_3$): δ (ppm) 1.53, 2.45, 2.50, 2.68 (s, 6:3:3:6 H, Tp′CH_3); 5.73, 6.10 (s, 2:1 H, Tp′*H*); 6.87, 7.04, 7.21 (m, 2:2:1 H, phenyl-*H*). ^{13}C NMR (CDCl$_3$): δ (ppm) 13.3, 14.0, 17.9, 18.1 (2:1:2:1 Tp′*C*H$_3$); 107.4, 110.5 (2:1 Tp′*C*H); 128.3, 129.2, 129.4 (1:2:2 phenyl-*C*); 145.6, 149.2, 151.9, 163.3 (2:1:2:1 Tp′*C*-CH$_3$); 174.9 (S–C–phenyl); 248.0 ($^1J_{W-C}$ = 162 Hz, *C*O). Anal. Calcd for C$_{23}$H$_{27}$BN$_6$O$_2$SW: C, 42.74; H, 4.22; N, 13.00. Found: C, 42.50; H, 4.25; N, 12.80.

Preparation of Tp′W(CO)$_2$(S^{i}Pr) (6). A slight excess of ^{i}PrSH was added to a THF solution (40 mL) of Tp′W(CO)$_2$I (662 mg, 1 mmol). After stirring overnight, the solution volume was reduced to about 10 mL. The product was filtered onto an alumina column and eluted with CH$_2$Cl$_2$. The solvent was then evaporated, and recrystallization from CH$_2$Cl$_2$/hexanes at −30 °C followed by a second recrystallization from slow diffusion of hexane into a CH$_2$Cl$_2$ solution resulted in an analytically pure crystalline solid containing two isomers in a 2:1 ratio. Yield: 58%. IR (KBr): ν_{CO} (cm^{-1}) 1927, 1811. IR (THF): ν_{CO} (cm^{-1}) 1935, 1821. ^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) 1.10 (d, $^3J_{H-H}$ = 6.8 Hz, minor isomer SCH(CH_3)$_2$); 1.54 (d, $^3J_{H-H}$ = 6.8 Hz, major isomer SCH(CH_3)$_2$); 1.83, 1.89, 2.26, 2.40, 2.42, 2.46, 2.66 (s, Tp′CH_3); 2.88 (m, $^3J_{H-H}$ 6.8 Hz, minor isomer SC*H*(CH$_3$)$_2$); 4.84 (m, $^3J_{H-H}$ = 6.8 Hz, major isomer SC*H*(CH$_3$)$_2$); 5.91, 5.92, 6.06 (s, Tp′*H*). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 12.6, 13.2, 17.0, 17.8, 19.7, 22.4, 24.0 (Tp′*C*H$_3$ and SCH(*C*H$_3$)); 72.7, 76.1 (minor and major isomer S*C*H(CH$_3$)); 106.7, 107.0, 109.3 (Tp′*C*H); 145.5, 146.0, 148.6, 149.6, 151.7, 152.7, 161.7, 162.1 (Tp′*C*-CH$_3$); 251.3 ($^1J_{W-C}$ = 163 Hz, minor isomer *C*O); 254.4 ($^1J_{W-C}$ = 164 Hz, major isomer *C*O). Anal. Calcd for C$_{20}$H$_{29}$BN$_6$O$_2$SW: C, 39.24; H, 4.77; N, 13.78. Found: C, 39.35; H, 4.82; N, 13.78.

Preparation of Tp′W(CO)$_2$(SCH$_2$Ph) (7). To a solution of Tp′W(CO)$_2$I (700 mg, 1.06 mmol) in CH$_2$Cl$_2$ (50 mL) was added an excess of PhCH$_2$SH. The solution was stirred overnight. The solvent was removed in vacuo, and the product was eluted through an alumina column with toluene. Solvent was again evaporated under vacuum, and the remaining orange solid was then washed with hexanes, filtered, and dried. The solid was then recrystallized by the slow diffusion of hexanes into a THF solution. Analytically pure crystals formed. Yield: 436 mg (63%). IR (KBr): ν_{CO} (cm^{-1}) 1923, 1796. IR (THF): ν_{CO} (cm^{-1}) 1937, 1827. ^{1}H NMR (CD$_2$Cl$_2$): δ (ppm) 1.75, 2.40, 2.41, 2.67 (s, 6:3:3:6 H, Tp′CH_3); 2.87 (s, 2H, SCH_2); 5.95 and 6.10 (s, 2:1 H, Tp′*H*); 6.99, 7.13, 7.25 (m, 2:2:1 H phenyl-*H*). ^{13}C NMR (CD$_2$Cl$_2$): δ (ppm) 12.6, 13.2, 17.1, 17.8 (2:1:2:1 Tp′*C*H$_3$); 77.3 (S*C*H$_2$); 106.9, 109.8 (2:1 Tp′*C*H); 126.9, 128.6, 129.0 (1:2:2 phenyl-*C*); 141.2 (S-C-phenyl); 145.8, 149.1, 151.1, 162.7 (1:2:1:2 Tp′*C*-CH$_3$); 251.3 ($^1J_{W-C}$ = 162 Hz, *C*O). Anal. Calcd for C$_{24}$H$_{29}$BN$_6$O$_2$SW: C, 42.74; H, 4.22; N, 13.00. Found: C, 42.50; H, 4.25; N, 12.80.

Thiolate Exchange Reactions: Tp′W(CO)$_2$(SPh) with NaSMe. To a flask containing Tp′W(CO)$_2$(SPh) (125 mg) and a 6-fold excess of NaSMe was added 20 mL of THF. The reaction was stirred overnight. After 12 h, a color change from orange to yellow had occurred, and an IR spectrum showed a slight change in the frequencies of the CO-stretching bands consistent with formation of Tp′W(CO)$_2$(SMe). The solution was filtered, and the solvent was evacuated under vacuum. Formation of Tp′W(CO)$_2$(SMe) was confirmed by ^{1}H NMR, which showed nearly quantitative conversion. Yield: (95 mg) 85%.

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Table I. Crystallographic Data Collection Parameters

	$Tp'W(CO)_2$-$(S$-$pC_6H_4NO_2)$	$Tp'W(CO)_2$-(SCH_2Ph)
chemical formula	$WC_{23}BN_7O_4H_{26}S\cdot{}^1/_2CH_2Cl_2$	$WC_{24}H_{29}BO_2SN_6$
fw	733.68	660.24
space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.518(2)	9.709(2)
b, Å	12.016(5)	10.230(2)
c, Å	13.904(3)	15.355(3)
α, deg	77.25(3)	72.92(2)
β, deg	76.44(2)	84.32(2)
γ, deg	64.23(2)	62.87(1)
Z	2	2
V, Å^3	1524.1(8)	1296.3(4)
d_{calcd}, g/cm^3	1.599	1.692
λ, Å	0.70930	0.70930
μ, cm^{-1}	40.6	46.6
transm coeff	N/A	0.365–0.375
R^a	0.044	0.047
$R_w{}^b$	0.065	0.057

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

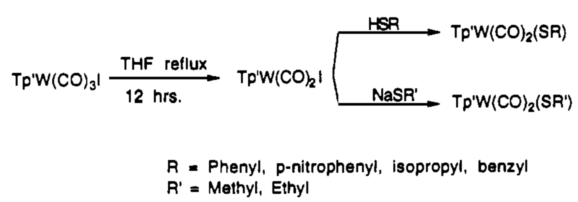
$Tp'W(CO)_2(S^iPr)$ with NaSPh. To a THF slurry of NaH (1 g) was added a slight excess of PhSH. The solution was stirred for 1 h and was then filtered, leaving a white powder. To this white powder was added a THF solution of $Tp'W(CO)_2(S^iPr)$ (125 mg). The mixture was stirred for 3 h at which time the IR spectrum showed a slight change in the frequencies of the CO-stretching bands consistent with the formation of $Tp'W(CO)_2(SPh)$. The solution was filtered and solvent was removed under vacuum. A ^1H NMR spectrum confirmed quantitative formation of $Tp'W(CO)_2(SPh)$.

X-ray Diffraction Data Collection for $Tp'W(CO)_2(S$-p-$C_6H_4NO_2)$ (4) and $Tp'W(CO)_2(SCH_2Ph)$ (7). Crystals of 4 were grown by slow diffusion of a concentrated CH_2Cl_2 solution into MeOH and for 7 by slow diffusion of a THF solution into hexanes. For 4 a red block of approximate dimensions 0.30 × 0.30 × 0.30 mm was selected and mounted on a glass wand coated with epoxy. For 7 a yellow-orange block of approximate dimensions 0.30 × 0.30 × 0.30 mm was selected and mounted on a glass wand coated with epoxy. Single-crystal data were collected on a Rigaku AFC6s automated diffractometer. For 4 50 centered reflections found in the region $40.0° < 2\theta < 45.0°$ indicated a triclinic cell. For 7 49 centered reflections found in the region $40.0° < 2\theta < 50.0°$ indicated a triclinic cell. Details of the data collection for both crystals are reported in Table I. Diffraction data were collected with h from -9 to $+11$, k from 0 to 12 and l from -14 to $+14$ for 4 and h from -10 to $+11$, k from 0 to 12 and l from -16 to $+18$ for 7 under the conditions specified in Table I. In both cases only data with $I > 2.5\sigma(I)$ were used in the structure solutions and refinements. No absorption correction was made for 4. Absorption corrections were made for 7. In both cases the data were corrected for Lorentz–polarization effects in the final stages of data reduction.

Space group $P\bar{1}$ was confirmed for both 4 and 7, and the positions of the tungsten and the sulfur atoms were deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations using the NRCVAX[19] system. During the refinement of the S-p-$C_6H_4NO_2$ structure an average of one-half molecule of CH_2Cl_2 was found in the asymmetric unit of the crystal.

The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å, and these hydrogens were then given an isotropic thermal parameter 0.1 greater than that of the associated atom. Final least-squares refinement of 4 resulted in residuals $R = 0.044$ and $R_W = 0.065$. The final Fourier map had no hole deeper than -1.37 e Å^{-3}, and no peak greater than $+1.99$ e Å^{-3}. Final least-squares refinement of 7 resulted in residuals $R = 0.047$ and $R_W = 0.057$. The final Fourier map had no hole deeper than -3.39 e Å^{-3}, and no peak greater than $+4.31$ e Å^{-3}.

Scheme I



Results and Discussion

Synthesis. A series of complexes of the type $Tp'W(CO)_2(SR)$ has been prepared by metathesis of thiolate reagents with $Tp'W(CO)_2I$ (Scheme I). Brown, paramagnetic $Tp'W(CO)_2I$ can be synthesized in good yield by refluxing $Tp'W(CO)_3I$ in THF overnight. This unsaturated 16-electron complex reacts with dioxygen to form $Tp'WO(CO)I$ if exposed to air[20]; it is suspected to be an intermediate in the reported reaction of $Tp'W(CO)_3I$ and oxygen which yields the same products.[18] Reaction of $Tp'W(CO)_2I$ with amines result in the formation of amido complexes of the type $Tp'W(CO)_2(NR_2)$, which display a rich chemistry at the amido ligand.[21] An interest in the synthesis, stucture, and properties of low-valent carbonyl thiolate complexes led us to explore the reactions of $Tp'W(CO)_2I$ with thiolates.

The title thiolate complexes were synthesized in good yield (58–87%) by stirring a CH_2Cl_2 or THF solution of $Tp'W(CO)_2I$ with the appropriate thiol or sodium thiolate. Complexes have been prepared from NaSMe, NaSEt, HS^iPr, HSPh, HS-p-$C_6H_4NO_2$, and $PhCH_2SH$. Column chromatography on alumina using either CH_2Cl_2, THF, or toluene as eluent permitted purification of the complexes. Toluene is the preferred eluent because $Tp'WO(CO)I$, a common contaminant, will not elute with toluene. Recrystallization afforded analytically pure $Tp'W(CO)_2(SR)$ complexes (Scheme I); in some cases dichloromethane solvates are observed to form. The complexes are remarkably resistant to aerial oxidation, and they are surprisingly stable both thermally and chemically. The $Tp'W(CO)_2(SEt)$ complex was refluxed in toluene overnight without noticeable decomposition. The $Tp'W(CO)_2(S(p$-$C_6H_4NO_2))$ derivative was refluxed in toluene in the presence of 1-phenyl-propyne in an attempt to form $Tp'W(CO)(PhC{\equiv}CMe)(SR)$. No reaction occurred after refluxing for 24 h. Note that $Tp'W(CO)(MeC{\equiv}CMe)(SMe)$ has been synthesized by the reaction of $Tp'W(CO)(MeC{\equiv}CMe)(OTf)$ with NaSMe.[22]

We had previously attempted to synthesize $Tp'W(CO)_2(SR)$ complexes by ultraviolet irradiation of either $[Tp'W(CO)_3]^-$ or the 17-electron radical $Tp'W(CO)_3$ for as long as 24 h in CH_2Cl_2 in the presence of RSSR (R = Me, Ph). These reactions resulted in the formation of the $Tp'W(CO)_2(SR)$ complexes but only low yields were achieved.

X-ray Crystal Structure of $Tp'W(CO)_2\{S(p$-$C_6H_4NO_2)\}$ (4) and $Tp'W(CO)_2(SCH_2Ph)$ (7). The molecular structures of 4 and 7 are shown in Figures 1 and 2, respectively. Respective atomic position parameters for the complexes are listed in Tables II and III. Selected intramolecular bond distances and angles are listed in Tables IV and V for 4 and 7, respectively. In both complexes the coordination sphere of the tungsten is approximately octahedral with the nitrogen donors of the Tp' ligand occupying three coordination sites in a *fac* orientation.

The W–N distances to the pyrazole nitrogens (2.168(8), 2.216(7), and 2.208(7) Å for 4 and 2.181(5), 2.194(5), and 2.237(5) Å for 7) and the N–W–N bond angles (80.7(3), 81.2(3), and 87.2(3)° for 4 and 79.6(2), 81.2(2), and 87.4(2)° for 7) are

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(19) The following references are pertinent to the NRCVAX system. (a) Gabe, E. J.; Le Page, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384. (b) Flack, H. *Acta. Crystallogr.* **1983**, *A39*, 876. (c) Scattering Factors from: *International tables for X-ray Crystallography*; Kynoch Press, Birmingham, England; 1974; Vol. IV. (d) Johnson, C. K. ORTEP—A Fortran Thermal Ellipsoid Plot Program. Technical Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. Larson, A. C. *Crystallographic Computing*; Munksgaard: Copenhagen, 1970, p 293. (f) Le Page, Y. *J. Appl. Crystallogr.* **1988**, *21*, 983. (g) Le Page, Y.; Gabe, E. J. *J. Appl. Crystallogr.* **1979**, *12*, 464. (h) Rogers, D. *Acta Crystallgr.* **1981**, *A37*, 734.

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(21) Perez, P. J.; Luan, L.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 7928.

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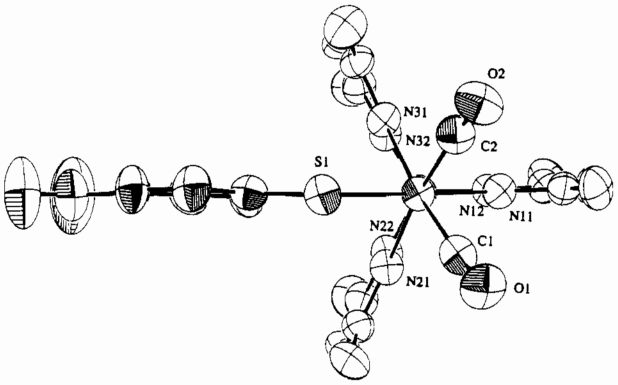

Figure 1. ORTEP diagram for Tp′W(CO)$_2$(S-*p*-C$_6$H$_4$NO$_2$).

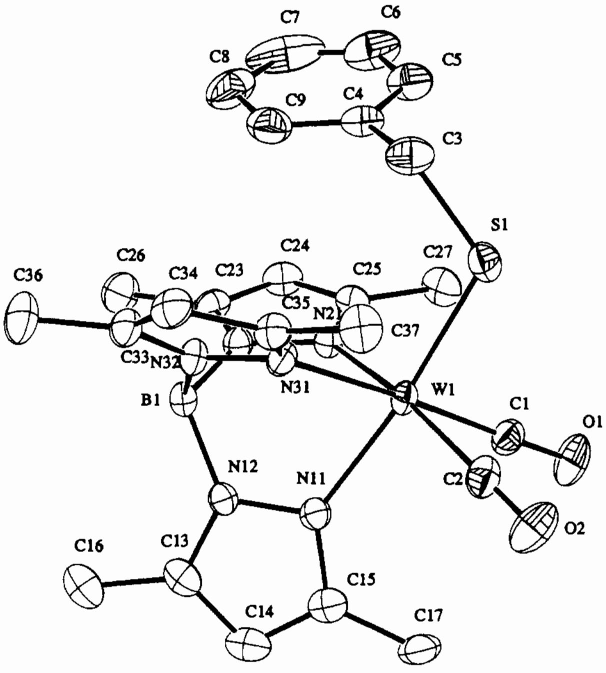

Figure 2. ORTEP diagram for Tp′W(CO)$_2$(SCH$_2$Ph).

comparable to values reported previously for related complexes.[23] The increased angle for N(21)–W–N(31) may reflect steric interactions between the rings containing these atoms and the SR group. The W–S bond distances, 2.320(2) (**4**) and 2.298(2) Å (**7**) are in between values reported for W–S single (2.4–2.5 Å) and double bonds (2.1 Å),[24] and near values reflecting some π donation from sulfur to metal.[24]

The W–S–C bond angles are both significantly distorted from linear at 116.8(3) and 114.7(3)° for **4** and **7**, respectively. This bending is indicative of significant lone-pair donation from one of the two lone pairs on sulfur.

One somewhat surprising structural feature of these complexes is that the *p*-nitrophenyl substituent in **4** and the benzyl substituent in **7** are oriented up towards the Tp′ ring as opposed to the seemingly sterically less crowded position away from the Tp′ ligand. Furthermore, in the benzyl case the phenyl ring is proximal to the Tp′ ligand, and the plane containing the phenyl ring lies parallel to the plane of one of the pyrazole rings for both complexes. For complexes of the type Tp′W(CO)(I)(PhC≡CR) (R = H, Me) it was also found that the predominant isomer had the phenyl substituent up between two of the pyrazole rings.[17] In the alkyne case it was suggested that this might be due to an electronic effect, namely some weak attractive π-interaction between the phenyl ring and the pyrazole ring. The fact that a second isomer was detected for only the bulky ^{i}Pr complex in this series of thiolate complexes leads us to believe that the structures for the SMe and SEt complexes have the alkyl group proximal to the Tp′ ring. This is compatible with the intuitive notion that the ^{i}Pr group is forced down for steric reasons, and thus we observe two isomers only for this bulky substituent. It appears that NMR chemical shifts are moved upfield for groups that approach the Tp′ ring. If this holds true for the present case, then the major isomer of the ^{i}Pr complex has the alkyl group distal to Tp′. The results here reinforce the previous conclusions in that only the "up" isomer is observed for the complexes with aryl substituents. Furthermore, it seems that even the alkyl groups prefer to be oriented proximal to the Tp′ ring.[25] This may be an electronic effect rather than a steric one, but we have no good explanation. Regardless, it is possible to rank the preference of the substituents to be oriented toward the Tp′ rings as follows:

aryl > hydrogen > alkyl > lone pair of electrons

The two carbonyl ligands in both structures are drawn together, significantly deviating from the idealized octahedral angle of 90° (75.1(4)° for **4** and to 73.6(3)° for **7**). This acute OC–M–CO angle was also observed for the electronically similar Tp′W(CO)$_2$[N(H)(Tosyl)][26] complex, where the two carbonyl

Table II. Atomic Positional Parameters for Tp′W(CO)$_2$(S-*p*C$_6$H$_4$NO$_2$)

	x	*y*	*z*	B_{iso},[a] Å^2
W1	0.13273(3)	0.17465(3)	0.16889(2)	3.46(3)
S1	0.1787(3)	0.2075(2)	0.3132(2)	4.4(1)
C1	0.300(1)	0.008(1)	0.1761(7)	4.5(6)
O1	0.3976(8)	−0.0814(7)	0.1758(6)	6.0(4)
C2	0.299(1)	0.2089(9)	0.0960(8)	4.8(5)
O2	0.4058(7)	0.2198(7)	0.0567(6)	6.0(4)
C3	0.028(1)	0.2888(9)	0.3988(7)	4.2(5)
C4	−0.116(1)	0.3234(9)	0.3893(7)	4.8(5)
C5	−0.222(1)	0.385(1)	0.4607(7)	5.2(5)
C6	−0.192(1)	0.4081(9)	0.5416(7)	5.2(6)
C7	−0.054(1)	0.374(1)	0.5539(8)	5.6(6)
C8	0.054(1)	0.316(1)	0.4798(8)	5.6(6)
N9	−0.312(1)	0.468(1)	0.6204(7)	6.7(6)
O10	−0.432(1)	0.501(1)	0.6087(9)	11.6(8)
O11	−0.281(1)	0.487(1)	0.6913(7)	10.4(8)
B1	−0.191(1)	0.265(1)	0.1220(8)	3.8(5)
N11	0.062(8)	0.1562(7)	0.0391(6)	3.8(4)
N12	−0.774(7)	0.2009(6)	0.0347(5)	3.6(4)
C13	−0.90(1)	0.1840(8)	−0.542(6)	4.0(5)
C14	0.046(1)	0.1239(9)	−0.1050(7)	4.9(5)
C15	0.1401(9)	0.1083(8)	−0.0469(6)	3.9(4)
C16	−0.235(1)	0.232(1)	−0.0867(7)	5.7(6)
C17	0.298(1)	0.051(1)	−0.0713(8)	5.3(5)
N21	−0.0401(7)	0.1125(7)	0.2449(5)	3.8(4)
N22	−0.1724(7)	0.1716(6)	0.2180(5)	3.8(4)
C23	−0.264(1)	0.1276(9)	0.2790(7)	4.4(5)
C24	−0.185(1)	0.0358(9)	0.3494(7)	4.7(5)
C25	−0.049(1)	0.0301(8)	0.3273(6)	4.0(4)
C26	−0.417(1)	0.177(1)	0.2727(9)	6.1(6)
C27	0.057(1)	−0.055(1)	0.3781(7)	5.4(6)
N31	−0.0361(7)	0.3642(6)	0.1448(5)	3.8(4)
N32	−0.1699(7)	0.3775(6)	0.1345(5)	3.7(3)
C33	−0.261(1)	0.4995(8)	0.1278(7)	4.3(5)
C34	−0.178(1)	0.5629(9)	0.1324(8)	5.4(6)
C35	−0.043(1)	0.4782(8)	0.1419(6)	4.0(5)
C36	−0.414(1)	0.547(1)	0.1167(9)	5.9(6)
C37	0.076(1)	0.507(1)	0.1506(9)	6.1(7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

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(23) For example: Philipp, C. C.; White, P. S., Templeton, J. L. *Inorg. Chem.* **1992**, *31*, 3825.

(24) For example: (a) Feng, S. G.; Gamble, A. S.; Templeton, J. L. *Organometallics* **1989**, *8*, 2024. (b) Young, C. G.; Bruck, M. A.; Enemark, J. H. *Inorg. Chem.* **1992**, *31*, 593. (c) Burrow, T. E.; Hills, A.; Hughes, D. L.; Lane, J. D.; Morris, R. H.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1813. (d) Ellis, S. R.; Collison, D.; Garner, C. D.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1986**, 1483. (e) Bishop, P. T.; Dilworth, J. R.; Hutchison, J.; Zubieta, J. A. *Inorg. Chim. Acta.* **1984**, *84*, 115.

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Table III. Atomic Positional Parameters for Tp′W(CO)$_2$(SCH$_2$Ph)

	x	*y*	*z*	B_{iso},[a] Å^2
W1	0.40672(3)	0.02616(3)	0.23266(1)	2.59(1)
S1	0.2869(2)	0.0102(2)	0.1171(1)	3.8(1)
C1	0.4725(8)	−0.1905(8)	0.2899(6)	3.8(4)
O1	0.5185(8)	−0.3240(6)	0.3183(5)	5.9(4)
C2	0.6138(9)	−0.0837(8)	0.1857(5)	4.0(4)
O2	0.7340(7)	−0.1555(8)	0.1643(5)	6.0(3)
C3	0.124(1)	0.192(1)	0.0562(5)	4.8(5)
C4	−0.0210(8)	0.2448(9)	0.1111(5)	3.9(4)
C5	−0.110(1)	0.167(1)	0.1317(6)	5.2(5)
C6	−0.241(1)	0.215(1)	0.1758(7)	6.7(6)
C7	−0.292(1)	0.346(2)	0.2006(7)	9.5(9)
C(8)	−0.210(1)	0.430(1)	0.1812(7)	7.4(6)
C9	−0.069(1)	0.377(1)	0.1353(6)	5.1(5)
B1	0.2652(9)	0.3337(9)	0.3066(5)	3.0(4)
N11	0.5039(6)	0.0732(6)	0.3353(4)	2.9(3)
N12	0.4279(6)	0.2145(6)	0.3527(4)	2.8(3)
C13	0.5080(9)	0.2202(9)	0.4164(5)	3.6(4)
C14	0.6382(9)	0.0802(1)	0.4418(5)	4.2(4)
C15	0.6339(8)	−0.0067(8)	0.3913(5)	3.6(3)
C16	0.464(1)	0.361(1)	0.4451(6)	5.0(5)
C17	0.7501(9)	−0.1658(9)	0.3898(7)	4.9(4)
N21	0.2016(6)	0.1173(6)	0.3120(4)	2.8(3)
N22	0.1561(6)	0.2554(6)	0.3298(4)	3.0(3)
C23	0.0258(8)	0.2898(9)	0.3749(5)	3.4(3)
C24	−0.0153(8)	0.174(1)	0.3874(5)	4.0(4)
C25	0.0957(8)	0.0697(8)	0.3472(5)	3.2(3)
C26	−0.059(1)	0.438(1)	0.4009(7)	5.4(5)
C27	0.105(1)	−0.078(1)	0.3427(6)	4.6(5)
N31	0.3560(6)	0.2686(6)	0.1603(4)	2.9(3)
N32	0.2835(6)	0.3805(6)	0.2032(4)	3.0(3)
C33	0.2622(8)	0.5167(8)	0.1453(5)	3.5(4)
C34	0.3207(9)	0.4914(8)	0.0645(5)	3.8(4)
C35	0.3825(8)	0.3350(7)	0.0753(4)	3.1(3)
C36	0.185(1)	0.6634(9)	0.1712(7)	5.4(5)
C37	0.468(1)	0.2490(9)	0.0076(5)	4.1(4)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Tp′W(CO)$_2$(S-*p*-C$_6$H$_4$NO$_2$)

W–S1	2.320(2)	W–N31	2.208(7)
W–C1	2.01(1)	S1–C3	1.78(1)
W–C2	1.97(1)	C1–O1	1.12(1)
W–N11	2.168(7)	C2–O2	1.18(1)
W–N21	2.216(7)		

S1–W–C1	88.8(3)	C1–W–N31	173.3(3)
S1–W–C2	87.9(3)	C2–W–N11	96.3(4)
S1–W–N11	173.9(2)	C2–W–N21	172.8(3)
S1–W–N21	95.5(2)	C2–W–N31	98.9(3)
S1–W–N31	93.9(2)	N11–W–N21	80.7(3)
C1–W–C2	75.1(4)	N11–W–N31	81.2(3)
C1–W–N11	96.4(3)	N21–W–N31	87.2(3)
C1–W–N21	98.6(3)	W–S1–C3	116.8(3)

Table V. Selected Bond Distances (Å) and Angles (deg) for Tp′W(CO)$_2$(SCH$_2$Ph)

W–S1	2.298(2)	W–N31	2.237(5)
W–C1	1.941(8)	C1–O1	1.178(9)
W–C2	1.989(8)	C2–O2	1.137(9)
W–N11	2.181(5)	S1–C3	1.851(9)
W–N21	2.194(5)	C3–C4	1.52(1)

S1–W–C1	88.8(2)	C2–W–N11	92.6(3)
S1–W–C2	91.0(2)	C2–W–N21	168.2(3)
S1–W–N11	172.6(2)	C2–W–N31	100.3(3)
S1–W–N21	97.7(1)	N11–W–N21	79.6(2)
S1–W–N31	91.8(1)	N11–W–N31	81.2(2)
C1–W–C2	73.6(3)	N21–W–N31	87.4(2)
C1–W–N11	98.3(3)	W–S1–C3	114.7(3)
C1–W–N21	98.6(3)	S1–C3–C4	114.4(6)
C1–W–N31	173.8(3)		

ligands subtend an angle of 74.1°. Inspection of the ORTEP diagrams of these complexes suggest that this OC–M–CO angle results from an electronic effect as opposed to a steric one.

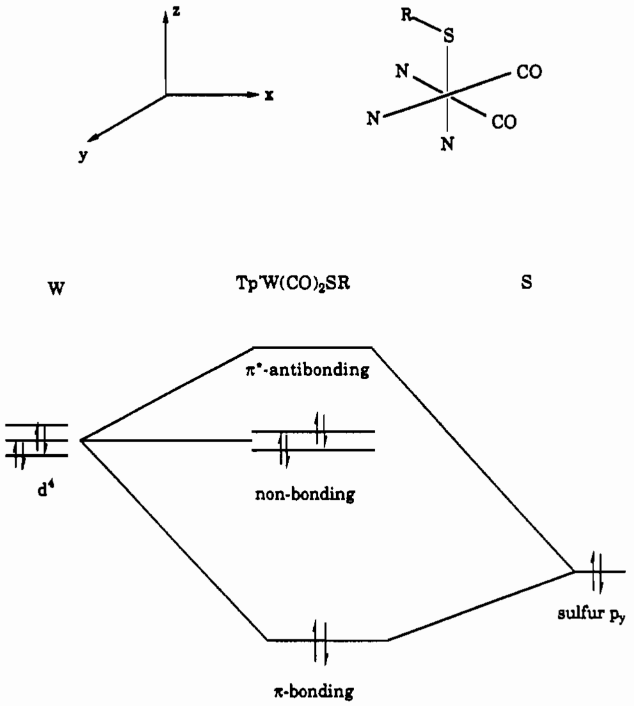

Figure 3. Molecular orbital diagram for Tp′W(CO$_2$)(SR) describing the metal–ligand π-bonding.

If the *z* axis is taken to be the axis of the W–S bond and the carbonyls are placed in the *xy* plane so that they lie between the $+x$ and $+y$ and the $+x$ and $-y$ axes, as shown in Figure 3, then discussion of the important π-interactions is simplified. The molecular orbital diagram reflecting the donation of one lone pair of electrons from the sulfur atom of the thiolate ligand is shown in Figure 3. Other π-interactions are ignored in this diagram. Since the tungsten is formally +2 and d^4, the two degenerate non-bonding dπ orbitals on the tungsten are filled and the LUMO is the vacant π-antibonding combination comprised largely of the d_{yz} orbital on tungsten. Although there are two lone pairs on the sulfur that could potentially donate to tungsten, the sp^2 hybridized lone pair is lower in energy than the lone pair housed in a p orbital. Thus, for both overlap and energy considerations, the filled p orbital is the one that is positioned to be a stronger π-donor to the metal.

Figure 4 shows the effect of turning on back-bonding from the d^4 metal center to the carbonyl ligands. The net effect of this is to lower the energy of all three dπ orbitals. Note that the $d_{x^2-y^2}$ orbital is selectively stabilized more than the d_{yz} and the d_{xz} orbitals as it lies in the horizontal plane between the two carbonyl ligands.

With the phenyl or benzyl group lying in the molecular mirror plane either up or down, and using the coordinate system defined, the filled sulfur p_y orbital can interact with the tungsten in a π-bonding manner. The empty metal based dπ orbital with the appropriate symmetry to overlap the p_y lone pair would be the d_{yz} orbital. The d_{xz} orbital is filled for the d^4 case, and it is of the correct symmetry to back-bond with the π* orbitals of the two carbonyls. Decreasing the angle between the two carbonyls increases overlap and maximizes the back-bonding effect as can be seen in Figure 5.

Alternatively, one can consider rotation of the phenyl group by 90° about the W–S bond. In this case, using the same coordinate system, the sulfur p_x orbital now houses the lone pair of electrons best able to π-bond to the tungsten. The d_{xz} orbital should be vacant in order to accept the electrons from the sulfur p_x orbital. That would leave the d_{yz} orbital filled and attractive for back-donation to the carbonyls. As seen in Figure 6, in order to optimize this back-bonding the carbonyl ligands should open to an obtuse angle. Whether these angular distortions occur in the OC–M–CO angle as the thiolate substituent rotates is a question we have not been able to address experimentally.

Another aspect of the orbital scheme appropriate for these complexes is that, due to the π-interaction with the thiolate ligand,

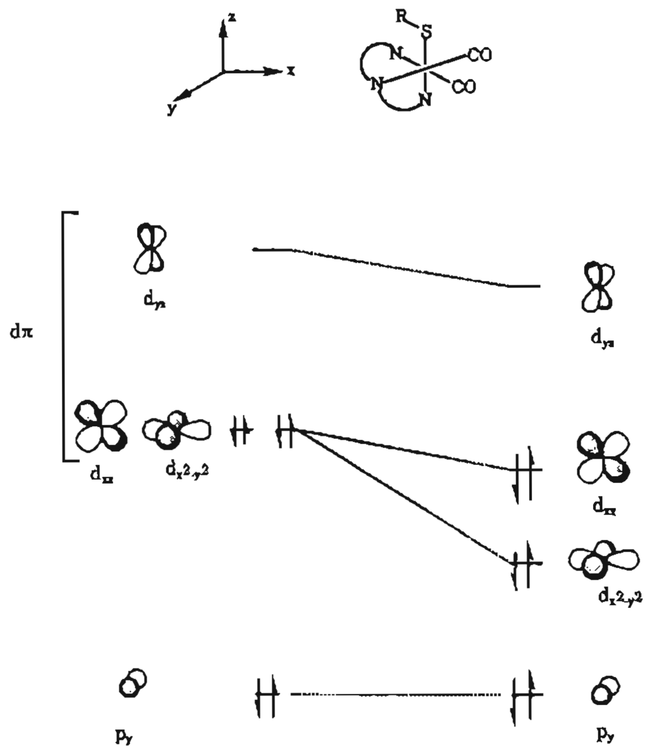

Figure 4. Change in molecular orbital diagram due to the contribution of back-bonding to the carbonyl ligands.

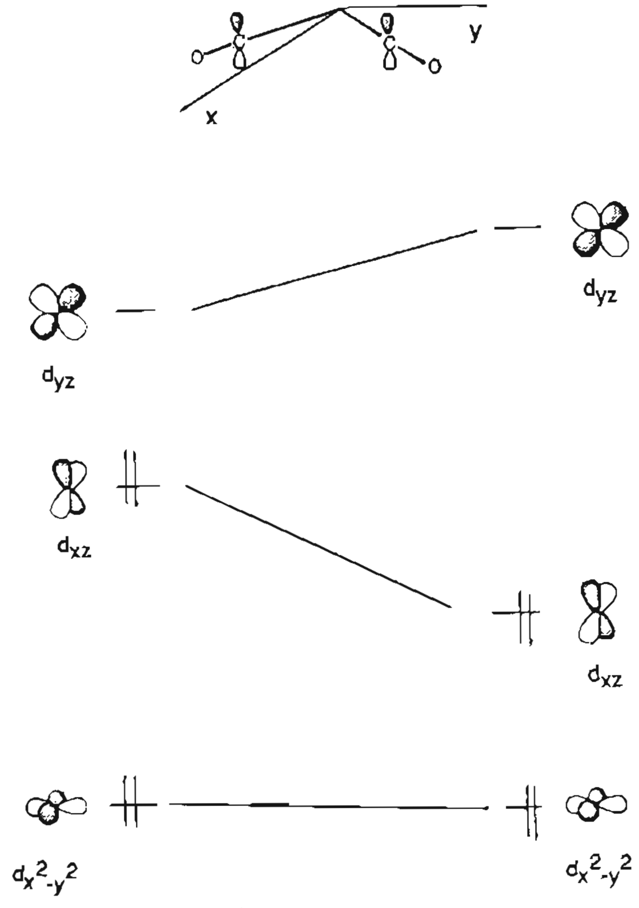

Figure 5. Stabilization of Tp'W(CO)$_2$(SR) by decreasing the angle between the two carbonyl ligands.

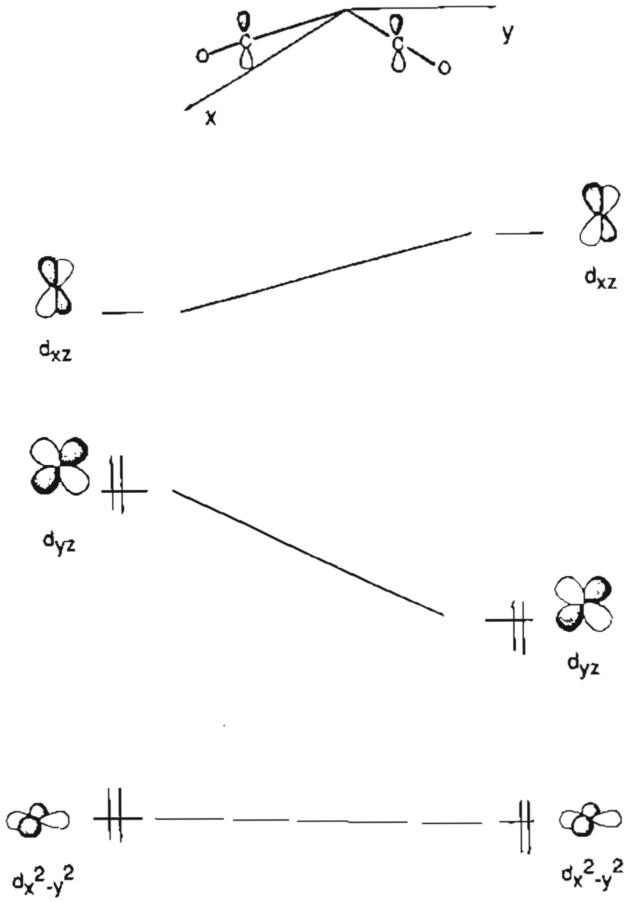

Figure 6. Stabilization of Tp'W(CO)$_2$(SR) by increasing the angle between the two carbonyl ligands.

Table VI. Selected IR Data

complex	IR ν_{CO}, cm^{-1} KBr	IR ν_{CO}, cm^{-1} THF	calcd θ, deg
Tp'W(CO)$_2$(SMe)	1930, 1813	1935, 1823	85
Tp'W(CO)$_2$(SEt)	1927, 1811	1935, 1823	82
Tp'W(CO)$_2$(SPh)	1933, 1923 1819, 1805	1937, 1827	80
Tp'W(CO)$_2$(S-*p*-C$_6$H$_4$NO$_2$)	1939, 1829 (br)	1942, 1834	79
Tp'W(CO)$_2$(S^{i}Pr)	1927, 1811	1933, 1819	81
Tp'W(CO)$_2$(SCH$_2$Ph)	1923, 1796	1937, 1827	81

Table VII. ν_{CO} for Selected Complexes

complex	ν_{CO}, cm^{-1}	ref
[Tp'W(CO)$_2$(NMe)][PF$_6$]	2083, 2006^a	21
[Tp'W(CO)$_2$(MeC≡CMe)][PF$_6$]	2055, 1974^a	17
[Tp'W(CO)$_2$(CPMe$_2$Ph)][PF$_6$]	2022, 1934^b	28
Tp'W(CO)$_2$(CH)	1986, 1899^c	29
Tp'W(CO)$_2$(I)	1944, 1846^c	this report
Tp'W(CO)$_2$(SMe)	1930, 1813^c	this report
Tp'W(CO)$_2$(OMe)	1923, 1796^c	22
Tp'W(CO)$_2$(NMe$_2$)	1904, 1777^c	21

^{a} In CH$_2$Cl$_2$. ^{b} In MeCN. ^{c} In THF.

the LUMO for these complexes is significantly lower than for related 18-electron compounds with σ^* LUMO properties. Thus, these complexes may be susceptible to attack by nucleophiles. The fact that we observe thiolate exchange reactions under mild conditions may reflect the accessibility of the LUMO. Since we were able to substitute alkonethiolates for arenethiolates and vice versa, we believe that these substitution reactions are driven toward equilibrium. Since the sodium thiolate reagent was present in large excess in both cases, it dictated the major product. We have no mechanistic data, but these substitutions may proceed by an associative mechanism involving attack of the thiolate lone pair on the d-orbital-based LUMO to form a seven-coordinate intermediate that could lose either of the thiolate ligands.

Spectral Properties. Pertinent infrared data are summarized in Table VI. The solid-state and solution carbonyl stretching frequencies provide some information about the donor properties of the thiolate ligands relative to other ligands in related tungsten dicarbonyl species (Table VII). If one considers the tungsten(II) fragment Tp'W(CO)$_2$$^+$ to require four electrons to count 18

Table VIII. Selected NMR Data

	^{1}H NMR, δ (ppm)			^{13}C NMR, δ (ppm)		
complex	Tp'*H*	Tp'*Me*	SCH_n	CO	$^1J_{W-C}$, Hz	S–*C*
Tp'W(CO)$_2$(SMe)	6.10 5.91	2.64, 2.41 2.41, 1.73	2.04	252.2	165	56.0
Tp'W(CO)$_2$(SEt)	6.08 5.89	2.62, 2.40 2.39, 1.74	1.74	252.2	166	65.7
Tp'W(CO)$_2$(S-*p*-C$_6$H$_4$NO$_2$)	6.09 5.70	2.66, 2.39 2.34, 1.43		247.2	162	179.9
Tp'W(CO)$_2$(SPh)	6.10 5.73	2.68, 2.50 2.45, 1.53		248.9	162	174.9
Tp'W(CO)$_2$(S^{i}Pr) (maj)	6.06 5.92	2.66, 2.46 2.26, 1.89	4.84	254.4	164	76.1
Tp'W(CO)$_2$(S^{i}Pr) (min)	6.06 5.91	2.66, 2.42 2.40, 1.83	2.88	251.3	163	72.7
Tp'W(CO)$_2$(SCH$_2$Ph)	6.10 5.95	2.67, 2.41 2.40, 1.75	2.87	251.3	164	77.3

at the metal, then the order of electron density provided by the sixth ligand as measured by the carbonyl ligand infrared stretching frequencies is shown below.

$$\mathrm{NMe} < \mathrm{MeC{\equiv}CMe} < \mathrm{CPMe_2Ph^-} < \mathrm{CH^-} < \mathrm{I^-} < \mathrm{SMe^-} < \mathrm{OMe^-} < \mathrm{NMe_2^-}$$

Another interesting feature of the IR spectra is the relative intensities of the two bands. The symmetric stretching band at high energy is significantly more intense than the lower energy asymmetric absorption. The intensities of the symmetric and asymmetric stretches reflect the angle θ between the two carbonyls via the following equation:[27]

$$\theta = 2\ \mathrm{arccot}\ (I_s/I_a)^{1/2} \qquad (1)$$

Here I_s is the intensity of the symmetric carbonyl stretch and I_a is the intensity of the asymmetric carbonyl stretch. Table VI lists the calculated OC–M–CO angles for the thiolate complexes dissolved in THF. The calculated angles are all significantly below 90° in agreement with the values found in the solid-state X-ray structures of the *p*-nitrophenyl (**4**) and benzyl (**7**) derivatives. With the exception of the benzyl complex, the angle between the carbonyls decreases as the electron-donating ability of the group attached to the sulfur decreases. Due to the limited accuracy of these measurements, it is not apparent whether this trend is electronically significant or merely a coincidence. The KBr infrared spectrum of the phenyl derivative displays two sets of absorptions for the carbonyl stretches. We attribute this to solid-state effects splitting the two bands. The asymmetric carbonyl stretch of the benzyl derivative in the solid state spectrum is at a significantly lower energy (10–30 cm^{-1}) than for the rest of the complexes in this study, but the origin of this shift is unknown.

The NMR data for all of the thiolate complexes are summarized in Table VIII. The ^{1}H NMR spectrum for each complex shows a 2:1 pattern for the Tp' resonances. This reflects molecular mirror symmetry. The ^{13}C NMR spectra also display a 2:1 pattern for the Tp' resonances. For the alkylthio complexes the resonance for the carbon bonded to the sulfur appeared at 56.0 ppm for the SMe, at 65.7 ppm for the SEt, at 72.7 ppm for the minor isomer of the S^{i}Pr, at 76.1 ppm for the major isomer and at 77.3 ppm for the benzyl complex. No two-bond coupling was evident from tungsten to these carbons. For the isopropyl and ethyl derivatives, 2D-COSY experiments were performed to determine the chemical shifts of the protons α to the sulfur. In the ethyl case these were found under one of the Tp'Me signals.

It is noteworthy that the Tp'W(CO)$_2$(S^{i}Pr) product exists as two isomers, presumably differing in the orientation of the alkyl group, i.e. propyl up and propyl down isomers. These isomers were observed in a 2:1 ratio in the ^{1}H NMR spectrum. None of the other complexes showed detectable amounts (by NMR) of a second isomer. Upon warming a sample of the two isomers in toluene-d_8, only one set of resonances was seen for this complex. We attribute the dynamic NMR results to rapid rotation around the W–S bond. The ΔG^* for this rotation was calculated from the observed rate constants. The average ΔG^* at $T = T_c$ using four different resonances was calculated to be 16.4 ± 0.5 kcal/mol. The average ΔG^* at $T < T_c$ using seven different signals was calculated to be 16.6 ± 0.3 kcal/mol. Thus, a value of ΔG^* = 16.5 kcal/mol characterizes this rearrangement.

Summary. Tungsten thiolate complexes of the general form Tp'W(CO)$_2$(SR) have been characterized spectroscopically by IR, ^{1}H NMR, and ^{13}C NMR and by elemental analysis. Single-crystal x-ray structures were obtained for the (*p*-nitrophenyl)-thio and benzylthio derivatives. The structures of these complexes have several noteworthy features. First, the angle between the two carbonyl ligands has been reduced significantly below 90°, and this acute angle has been rationalized with a molecular orbital explanation. Second, the aryl and alkyl substituents on the sulfur ligands of these complexes are located near sp^2 expectations indicating that there is significant donation of the sulfur p-based lone pair of electrons. Furthermore, in both cases the nitrophenyl and benzyl groups are proximal rather than distal to the bulky Tp' ligand. This affinity for phenyl rings to be near the Tp' ligand has been recognized previously. More surprising was that when R is methyl or ethyl, only one isomer is observed and the favored isomer appears to have the alkyl group bent toward the Tp' ligand. The ^{i}Pr derivative displayed two isomers; presumably they are the up and down locations of the propyl group relative to the Tp'. We believe that this is due to the steric bulk of the isopropyl group.

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Supplementary Material Available: Tables of bond distances and angles and anisotropic temperature factors and figures showing the structure of 4 and 7 (10 pages). Ordering information is given on any current masthead page.

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