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# $\pi$-Acid/$\pi$-Base Carbonyloxo, Carbonylsulfido, and Mixed-Valence Complexes of Tungsten

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Carbonyloxotungsten(IV) complexes, $Tp^*WOX(CO)$, are produced in the reactions of dioxygen (for X = Cl, Br, I) or pyridine *N*-oxide [for X = $S_2P(OPr^i)_2$, $S_2PPh_2$] with $Tp^*WX(CO)_2$ [Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)-borate]. Analogous carbonylsulfidotungsten(IV) species, $Tp^*WSX(CO)$, result from the reactions of $Tp^*WX(\kappa^2\text{-MeCN})(CO)$ with propylene sulfide. The carbonyloxo complexes exhibit $\nu$(CO) and $\nu$(W=O) IR bands in the 1995–1965 and 957–951 $cm^{-1}$ regions, respectively; the $\nu$(CO) and $\nu$(W=S) bands of the carbonylsulfido species appear at 1970–1937 and 512–502 $cm^{-1}$, respectively. The complexes possess $C_1$ symmetry and display carbonyl $^{13}C$ NMR resonances at $\delta$ 272–287, with $J_{WC}$ 160–196 Hz. The crystal structures of $Tp^*WO(S_2PPh_2)(CO)$ and $Tp^*WS(S_2PPh_2)(CO){\cdot}0.5CHCl_3$ reveal distorted octahedral tungsten centers coordinated by a *fac* tridentate Tp* ligand and mutually cis, monodentate chalcogenido [$d(W{=}O) = 1.698(4)$ Å; $d(W{=}S) = 2.135(4)$ Å], carbonyl, and dithiophosphinato ligands. In refluxing toluene, $Tp^*WOI(CO)$ converts into purple, mixed-valence $Tp^*W^{III}I(CO)(\mu\text{-}O)W^{V}OITp^*$. The dinuclear complex contains a nearly linear [173.1(6)°] $\mu$-oxo bridge connecting disparate distorted octahedral tungsten centers. The metrical parameters and spectroscopic properties are consistent with the presence of a $W^{III}/W^{V}$ mixed-valence species, possessing a filled, delocalized three-center (W–O–W) $\pi$ bond and a localized (on $W^{III}$), filled $d_\pi$ orbital that back-bonds to the carbonyl ligand.

## Introduction

As a consequence of nd → $\pi^*$ back-bonding, $\pi$-acid ligands such as carbon monoxide avidly bind to electron-rich, low-valent metal centers.[1–3] Conversely, $\pi$-base terminal oxo ligands participate in $\pi \rightarrow$ nd interactions and preferentially bind to electron-deficient, high-valent metal centers.[4,5] Because of the conflicting $\pi$-bonding requirements of these "textbook" ligands, mononuclear carbonyloxo complexes are rarely stable.[6] Apart from the intrinsic appeal associated with their rarity and electronic novelty, there are important practical reasons for studying carbonyloxo and related $\pi$-acid/$\pi$-base complexes. One reason is the growing interest in the activation and utilization of carbon dioxide, a principal contributor to global warming. Metal-induced carboxyl-bond-cleavage reactions are known to produce carbonyl, oxo, or *carbonyloxo* complexes, depending on the oxophilicity of the metal.[7–9] The carbonyl and oxo (or oxygen atom) moieties can undergo additional reactions that could serve as the basis for catalytic processes to convert $CO_2$ into environmentally benign or useful chemicals. The interconversion of CO and $CO_2$ and the use of these and other C1 sources for chemicals and fuels are important strategies for environmentally sustainable technologies.[7–10] Carbonyloxo complexes are also putative intermediates in the oxidation of CO in catalytic converters and metal–oxide-catalyzed processes, e.g., methanol synthesis and the water

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gas shift reaction.[11,12] Carbonyl ligand displacement, redox, and group-transfer reactions of carbonyloxo complexes present significant opportunities for chemical synthesis (vide infra). The activation of dioxygen by transition metals, another facet of the chemistry described herein, is also an area of significant industrial and biological importance.[11−13]

Ternary carbonyloxo complexes are stable only in low-temperature matrixes or the gas phase. Group 6 carbonyloxo complexes, viz., *trans*-$MO_2(CO)_4$, $MO_2(CO)_3$, and $MO_2(CO)_2$ (M = Cr, Mo, W), are generated in methane or argon matrixes upon photolysis of $M(CO)_6$ in the presence of oxidants such as $O_2$, $CO_2$, or $N_2O$, with the ultimate products being metal oxides.[14] Complexes such as MO(CO) and $MO_2(CO)_2$ are the main species formed when group 6 atoms and $CO_2$ are codeposited in argon matrixes.[15] In the gas phase, complexes of the type $[MO_2(CO)_x]^-$ ($x = 3$ and 4) are observed when the anions $[M(CO)_5]^-$ encounter $O_2$,[16] whereas $Mo^+$, $MoO^+$, and $MoO_2{}^+$ react with $CO_2$ and CO to give species such as $[OMo(CO)]^+$ and $[MoO_2(CO)]^+$.[17] Carbonyloxo complexes of other metals have been produced using similar methods.[14] Mononuclear, ternary carbonylsulfido species are, to our knowledge, unknown.

The first stable carbonyloxo complexes were synthesized by Mayer and co-workers in the late 1980s.[18−22] These complexes, $MOCl_2(CO)L_2$ (M = Mo, W; L = $PMePh_2$, $PMe_3$), were prepared by two routes, viz., L/CO ligand exchange at $MOCl_2L_3$[18,20] or oxidative addition of $CO_2$ to $WCl_2L_4$.[19,20] The crystal structure of $WOCl_2(CO)(PMePh_2)_2$ revealed a distorted octahedral complex with a cis arrangement of oxo and carbonyl ligands [$d(W{=}O) = 1.689(6)$ Å, $d(W{-}C) = 2.029(9)$ Å, and $\angle(O{=}W{-}C) = 89.6(3)°$].[19,20] Reaction of $WSCl_2(PMePh_2)_3$ with CO or $WCl_2(PMePh_2)_4$ with COS yielded the carbonylsulfido complex, $WSCl_2(CO)(PMePh_2)_2$.[19,20] The bonding in these complexes involves back-donation to the π-acid carbonyl from a $(d_{xy})^2$ highest occupied molecular orbital orthogonal to the oxo ligand (whose π-base interactions involve the $d_{xz}$ and $d_{yz}$ orbitals, with $z$ along M=O).[20,22,23]

Carbonyloxotungsten(IV) complexes containing hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) were subsequently reported by the groups of Templeton and Young. Dinuclear, mixed-valence $Tp^*W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)Tp^*$[24] and mononuclear Tp*WOX(CO) (X = I, Br)[25] and $Tp^*WO(S_2PPh_2\text{-}S)(CO)$[26] were among the earliest examples. More recently, Tp*WOI(CO) has served as a useful precursor for carbonyloxo and organometallic oxo complexes. Thus, reaction with silver triflate provides access to $Tp^*WO(O_3SCF_3)(CO)$ and salts of $[Tp^*WO(NCMe)(CO)]^+$.[27] The crystal structure of $[Tp^*WO(NCMe)(CO)][B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$ revealed W=O and W−C distances of 1.781(4) and 2.080(6) Å, respectively, and an O=W−C angle of 91.35(20)°.[27] Complexes derived from Tp*WOI(CO) contain inter alia $\eta^2$-nitrile, amido, nitrile-coupled, alkyne, vinylidene, and carbene coligands.[27−29]

Mixed-valence complexes exhibit interesting optical, magnetic, and chemical properties that arise from the presence of different formal oxidation states and variable degrees of intermetallic electronic communication.[30] We are unaware of any confirmed reports of localized $W^{III}/W^{V}$ complexes. The compound $K_4[W_2(\mu\text{-}O)Cl_{10}]$ was initially described as a $W^{III}/W^{V}$ species,[31] but spectroscopic and magnetic data supporting an antiferromagnetically coupled $W^{IV}$ $d^2$ description were later presented.[32] The complex exhibits a symmetrical, binuclear structure with a linear W−O−W unit.[33] The $[M{-}O{-}M]^{n+}$ moiety is a common structural unit in transition-metal chemistry and is often present in mixed-valence species.[30,34]

This paper reports the synthesis and characterization of carbonyloxo- and carbonylsulfidotungsten(IV) complexes containing Tp*. It describes optimized syntheses, full characterization data, and details of the X-ray crystal structures of representative species, viz., $Tp^*WO(S_2PPh_2)(CO)$ and $Tp^*WS(S_2PPh_2)(CO)\cdot 0.5CHCl_3$. The structure of $Tp^*WS(S_2PPh_2)(CO)$ is the first for a mononuclear carbonylsulfido complex of any element. Aspects of this work have been communicated.[26] The synthesis and structure of mixed-valence $Tp^*W^{III}I(CO)(\mu\text{-}O)W^{V}OITp^*$, formed upon decarbonylation of Tp*WOI(CO), are also reported.

## Experimental Section

**Material and Methods.** All reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques. Samples of $Tp^*WX(CO)_x$ ($x = 2$, 3),[35,36] $Tp^*WX(\kappa^2\text{-}MeCN)(CO)$,[37] and $Tp^*W(S_2PR_2)(CO)_2$[38] were

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prepared by literature methods, and all other reagents were analytical reagent grade or better. The evolution of $CO_2$ in reactions was detected by passing the headspace gas through freshly prepared $Ca(OH)_2$ solutions (blanks were negative for $CO_2$). Solid-state (KBr disk) and solution ($CH_2Cl_2$) IR spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were obtained using Varian Unity 300 and Varian Unity Plus 400 spectrometers and referenced to internal $CHCl_3$ ($\delta_H$ 7.26; $\delta_C$ 77.36) and external 85% $H_3PO_4$ ($\delta$ 0.0). UV−visible spectra were recorded on a Hitachi 150-20 double-beam spectrophotometer. Microanalyses were performed by Atlantic Microlabs, Norcross, GA. Selected spectroscopic data are presented in Table 1. Complete $^{13}C$ NMR data are available as Supporting Information (Table S1).

**Syntheses. Tp*WOI(CO).** In a modification to the synthesis reported by Feng et al.,[25] a solution of Tp*WI$(CO)_2$ (0.22 g, 0.33 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature for 45 min under an atmosphere of dioxygen. The solvent was removed, and the residue was chromatographed on a silica gel column using dichloromethane as the eluent. The purple fraction was collected and reduced to dryness. The residue was recrystallized from dichloromethane/methanol to give dark purple crystals that were filtered, washed with methanol (5 mL), and dried in vacuo. Yield: 0.11 g, 51%. Spectroscopic properties were identical with those reported earlier.[25]

**Tp*WOBr(CO).** In a modification to the synthesis reported by Feng et al.,[25] a solution of Tp*WBr$(CO)_2$ (0.25 g, 0.41 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature for 30 min under an atmosphere of dioxygen. The reaction was worked up as described above for Tp*WOI(CO). Yield: 0.09 g, 35%.

Anal. Calcd for $C_{16}H_{22}BBrN_6O_2W$: C, 31.77; H, 3.67; N, 13.89. Found: C, 31.59; H, 3.70; N, 13.79. Spectroscopic properties were identical with those reported earlier.[25]

**Tp*WOCl(CO).** Prepared as described above for Tp*WBr(CO) using Tp*WCl$(CO)_2$ (0.33 g, 0.58 mmol) in tetrahydrofuran (10 mL). Yield: 0.11 g, 34%.

Anal. Calcd for $C_{16}H_{22}BClN_6O_2W$: C, 34.29; H, 3.96; N, 14.99; Cl, 6.33. Found: C, 34.35; H, 3.91; N, 15.02; Cl, 6.39. IR (KBr, $cm^{-1}$): $\nu$(BH) 2556, $\nu$(CN) 1544, $\nu$(WCl) 310 (also see Table 1).

**Tp*WO$\{S_2P(OPr^i)_2$-*S*$\}$(CO).** A solution of Tp*W$\{S_2P(OPr^i)_2\}$-$(CO)_2$ (2.44 g, 3.25 mmol) in tetrahydrofuran (30 mL) was cooled to 0 °C, and then pyridine *N*-oxide (0.50 g, 5.26 mmol) was added. The reaction mixture was stirred for 2 h, and the solvent was removed by rotary evaporation. The residue was column chromatographed on silica gel using dichloromethane as the eluent; the pink fraction was collected. The product was recrystallized from dichloromethane/hexane to give pink crystals that were filtered, washed with hexane (5 mL), and dried in vacuo. Yield: 1.59 g, 66%.

Anal. Calcd for $C_{22}H_{36}BN_6O_4PS_2W$: C, 35.79; H, 4.91; N, 11.38; S, 8.68. Found: C, 35.87; H, 4.97; N, 11.32; S, 8.72. IR (KBr, $cm^{-1}$): $\nu$(BH) 2554, $\nu$(CN) 1543, $\nu$(PO) 968, 985, $\nu$(P=S) 667, $\nu$(PS) 538 (also see Table 1).

**Tp*WO$(S_2PPh_2$-*S*)(CO).** A solution of Tp*W$(S_2PPh_2)(CO)_2$ (1.23 g, 1.56 mmol) in tetrahydrofuran (30 mL) was cooled to 0 °C, and then pyridine *N*-oxide (0.22 g, 2.31 mmol) was added. The reaction mixture was stirred for 2 h and then worked up as described above for Tp*WO$\{S_2P(OPr^i)_2$-*S*$\}$(CO), except for the use of 3:1 dichloromethane/*n*-hexane as the chromatographic eluent. Yield: 0.76 g, 63%.

Anal. Calcd for $C_{28}H_{32}BN_6O_2PS_2W$: C, 43.43; H, 4.17; N, 10.85; S, 8.28. Found: C, 43.21; H, 4.24; N, 10.96; S, 8.29. IR (KBr, $cm^{-1}$): $\nu$(BH) 2555, $\nu$(CN) 1542, $\nu$(P=S) 653, $\nu$(PS) 537 (also see Table 1).

**Tp*WSI(CO).** Propylene sulfide (0.35 mL, 4.47 mmol) was added to a stirred suspension of Tp*WI($\kappa^2$-MeCN)(CO) (1.00 g, 1.48 mmol) in acetonitrile (30 mL), and the reaction mixture was heated at 75 °C for 4 h. After removal of the solvent, the residue was column chromatographed on silica gel using dichloromethane as the eluent; the orange-brown band was collected. The product was recrystallized from dichloromethane/methanol to give orange crystals that were filtered, washed with methanol (5 mL), and dried in vacuo. Yield: 0.78 g, 79%.

Anal. Calcd for $C_{16}H_{22}BIN_6OSW$: C, 28.77; H, 3.32; N, 12.58; S, 4.80. Found: C, 29.01; H, 3.39; N, 12.48; S, 4.93. IR (KBr, $cm^{-1}$): $\nu$(BH) 2555, $\nu$(CN) 1544 (also see Table 1).

**Tp*WSBr(CO).** Propylene sulfide (0.2 mL, 2.55 mmol) was added to a stirred suspension of Tp*WBr($\kappa^2$-MeCN)(CO) (0.25 g, 0.40 mmol) in acetonitrile (10 mL), and the reaction mixture was heated at 75 °C for 8−9 h. The reaction was worked up as described above for Tp*WSI(CO), with the compound eluting as a green-brown band from the chromatography column. Yield: 0.17 g, 70%.

Anal. Calcd for $C_{16}H_{22}BBrN_6OSW$: C, 30.94; H, 3.57; N, 13.53; S, 5.16. Found: C, 30.94; H, 3.55; N, 13.30; S, 5.22. IR (KBr, $cm^{-1}$): $\nu$(BH) 2555 m, $\nu$(CN) 1544 m (also see Table 1).

**Tp*WSCl(CO).** Propylene sulfide (0.6 mL, 7.66 mmol) was added to a stirred suspension of Tp*WCl($\kappa^2$-MeCN)(CO) (1.00 g, 1.71 mmol) in acetonitrile (30 mL), and the reaction mixture was heated at 75 °C for 4 days. After removal of the solvent, the residue was column chromatographed (twice) on silica gel using dichloromethane as the eluent; the brown band was collected. The product was recrystallized from dichloromethane/methanol to give brown crystals that were filtered, washed with methanol (5 mL), and dried in vacuo. Yield: 0.35 g, 36%.

Anal. Calcd for $C_{16}H_{22}BClN_6OSW$: C, 33.33; H, 3.85; N, 14.58; S, 5.56. Found: C, 33.16; H, 3.87; N, 14.90; S, 5.36. IR (KBr, $cm^{-1}$): $\nu$(BH) 2556 m, $\nu$(CN) 1544 m (also see Table 1).

**Tp*WS$\{S_2P(OEt)_2$-*S*$\}$(CO).** Propylene sulfide (0.10 mL, 1.28 mmol) was added to a stirred suspension of Tp*W$\{S_2P(OEt)_2\}$-($\kappa^2$-MeCN)(CO) (0.50 g, 0.68 mmol) in acetonitrile (30 mL), and the reaction mixture was heated at 75 °C for 5 h. The reaction was worked up as described above for Tp*WSI(CO), with the compound eluting as a green band from the chromatography column. Yield: 0.22 g, 45%.

Anal. Calcd for $C_{20}H_{32}BN_6O_3PS_3W$: C, 33.07; H, 4.44; N, 11.57; S, 13.24. Found: C, 33.09; H, 4.45; N, 11.58; S, 13.18. IR (KBr, $cm^{-1}$): $\nu$(BH) 2562, $\nu$(CN) 1542, $\nu(PO_{alkyl})$ 941, $\nu$(P=S) 652, $\nu$(PS) 539 (also see Table 1).

**Tp*WS$\{S_2P(OPr^i)_2$-*S*$\}$(CO).** Propylene sulfide (0.15 mL, 1.92 mmol) was added to a stirred suspension of Tp*W$\{S_2P(OPr^i)_2\}$-($\kappa^2$-MeCN)(CO) (0.50 g, 0.63 mmol) in acetonitrile (30 mL), and the reaction mixture was heated at 75 °C for 5 h. The reaction was worked up as described above for Tp*WSI(CO), with the compound eluting as a green band from the chromatography column. Yield: 0.27 g, 55%.

Anal. Calcd for $C_{22}H_{36}BN_6O_3PS_3W$: C, 35.03; H, 4.81; N, 11.14; S, 12.75. Found: C, 35.08; H, 4.81; N, 11.04; S, 12.68. IR (KBr, $cm^{-1}$): $\nu$(BH) 2568, $\nu$(CN) 1542, $\nu(PO_{alkyl})$ 971, 987, $\nu$(P=S) 640, $\nu$(PS) 555 (also see Table 1).

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**Table 1.** Selected IR, NMR, and UV−Vis Spectral Data

| compound | IR,[a] cm$^{-1}$ | | $^1$H NMR, $\delta$ (CDCl$_3$) | | | $^{13}$CO NMR, $\delta$ (CDCl$_3$)[e] | $^{31}$P NMR, $\delta$ (CDCl$_3$) | UV−vis, $\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$) (CH$_2$Cl$_2$) |
|---|---|---|---|---|---|---|---|---|
| | $\nu$(CO) | $\nu$(W=E) | Tp* methyl[b] | Tp* methine[c] | coligand[d] | | | |
| Tp*WOI(CO)[f] | 1990 s, 1975 s | 953 m | 2.29, 2.38, 2.51, 2.57, 2.58, 2.91 | 5.70, 6.08, 6.26 | | 278.7 (189) | | 850 (40), 520 (130) |
| Tp*WOBr(CO)[f] | 1986 s, 1977 s | 957 m | 2.29, 2.36, 2.53, 2.56, 2.58, 2.87 | 5.71, 6.09, 6.24 | | 283.2 (194) | | 860 (30), 510 (155), 295 (7200) |
| Tp*WOCl(CO) | 1980 s, 1966 s | 951 m | 2.24, 2.36, 2.49, 2.50, 2.57, 2.90 | 5.63, 6.02, 6.16 | | 286.4 (195) | | 865 (25), 500 (165), 335 (1010) |
| Tp*WO{S$_2$P(OPr$^i$)$_2$}(CO) | 1997 s, 1994 s | g | 2.21, 2.41, 2.45, 2.49, 2.58, 2.94 | 5.59, 5.99, 6.13 | 1.38 (m, 12H), 4.93 (m, 2H) | 276.1 (191) | 115.1 | 820 (55), 485 (130) |
| Tp*WO(S$_2$PPh$_2$)(CO) | 1966 s, 1986 s | 952 m | 2.21, 2.29, 2.45, 2.49, 2.53, 2.81 | 5.56, 5.98, 6.14 | 7.35 (m, 6H), 8.07 (m, 4H) | 274.1 (196) | 83.7 | 810 (50), 510 (140) |
| Tp*WSI(CO) | 1961 s, 1943 s | 512 m | 2.22, 2.48, 2.61, 2.63, 2.82, 3.05 | 5.62, 6.13, 6.29 | | 273.1 (160) | | 1250 (45), 760 (155), 330 (4300) |
| Tp*WSBr(CO) | 1958 s, 1940 s | 502 m | 2.22, 2.46, 2.60, 2.64, 2.86, 3.03 | 5.62, 6.15, 6.26 | | 277.4 (163) | | 1290 (20), 745 (165) |
| Tp*WSCl(CO) | 1955 s, 1937 s | 502 m | 2.20, 2.42, 2.57, 2.63, 2.89, 2.99 | 5.60, 6.14, 6.23 | | 281.2 (165) | | 1260 (20), 975 (25), 735 (110) |
| Tp*WS{S$_2$P(OEt)$_2$}(CO) | 1967 s, 1955 s | 508 m | 2.18, 2.48, 2.55, 2.56, 2.82, 3.05 | 5.57, 6.10, 6.23 | 1.37 (t, 3H, $^3J = 7$), 1.41 (t, 3H, $^3J = 7$), 4.28 (m, 4H) | 272.6 (164) | 124.5 | 705 (160), 335 (5400) |
| Tp*WS{S$_2$P(OPr$^i$)$_2$}(CO) | 1970 s, 1959 s | 506 m | 2.17, 2.49, 2.54, 2.55, 2.82, 3.04 | 5.56, 6.08, 6.21 | 1.37 (d, 6H, $^3J = 6$), 1.38 (d, 3H, $^3J = 6$), 1.43 (d, 3H, $^3J = 6$), 4.94 (dsept, 1H), 4.99 (dsept, 1H) | 273.9 (165) | 126.2 | 705 (160), 340 (5020) |
| Tp*WS(S$_2$PPh$_2$)(CO) | 1967 s, 1959 s | 511 m | 2.19, 2.50, 2.54, 2.55, 2.74, 2.76 | 5.50, 6.06, 6.20 | 7.36 (m, 6H), 8.12 (m, 4H) | 272.8 (162) | 91.1 | 715 (140), 340 (5700) |
| Tp*WS{S$_2$PR$_2$)(CO), D1[h] | 1965 s, 1953 s | 506 m | 2.17, 2.49, 2.54, 2.55, 2.84, 3.02 | 5.55, 6.07, 6.20 | 0.8−2.6 (m, 36H), 4.31 (dq, 1H), 4.44 (dq, 1H) | 274.2 (165) | 133.7 | 700 (145), 350 (5300) |
| Tp*WS{S$_2$PR$_2$)(CO), D2[h] | 1965 s, 1962 s | 506 m | 2.17, 2.49, 2.54, 2.56, 2.82, 3.04 | 5.56, 6.07, 6.20 | 0.8−2.7 (m, 36H), 4.36 (dq, 1H), 4.48 (dq, 1H) | 275.3 (165) | 123.2 | 705 (155), 330 (3500) |
| Tp*WI(CO)($\mu$-O)WOITp* | 1870 s, 1878 s | 962 s | 1.15, 1.57, 2.29, 2.30, 2.31, 2.36, 2.41, 2.59, 2.71, 2.74, 2.82, 3.35 | 5.50, 5.60, 5.64, 5.79, 5.91, 6.12 | | 219.8 | | 520 (28500) |
| Tp*WO{S$_2$P(OPr$^i$)$_2$} | - | 943 s | 2.22, 2.54, 2.84 | 5.49 (1H), 6.03 (2H) | 1.37 (d, 6H, $^3J = 6$), 1.56 (d, 6H, $^3J = 6$), 5.09 (m, 2H, $^3J = 6$) | | | 578 (245), 330 (3330) |

[a] In KBr, except the first $\nu$(CO) value obtained from the CH$_2$Cl$_2$ solution spectrum. [b] All singlet resonances, each integrating for three protons. [c] All singlet resonances, each integrating for one proton (except the last entry). [d] Multiplicity, no. of H, and $J$ in Hz (where available) are given in parentheses. [e] Coupling constants, $J_{WC}$, in Hz are given in parentheses (see the Supporting Information for Table S1 of $^{13}$C NMR spectral data). [f] Some data reported in ref 25. [g] Obscured by ligand bands. [h] Diastereomer with R = O-(−)-menthyl.

**Table 2.** Crystallographic Data

| compd | $Tp^*WO(S_2PPh_2)(CO)$ | $Tp^*WS(S_2PPh_2)(CO)^a$ | $Tp^*WI(CO)(\mu\text{-}O)WOITp^{*b}$ |
|---|---|---|---|
| formula | $C_{28}H_{32}BN_6O_2PS_2W$ | $C_{28.5}H_{32.5}BCl_{1.5}N_6OPS_3W$ | $C_{31.5}H_{45}B_2ClN_{12}O_3I_2W_2$ |
| fw | 774.4 | 850.1 | 1318.4 |
| space group | $P\bar{1}$ | $Fdd2$ | $P\bar{1}$ |
| $a$, Å | 11.281(2) | 32.242(6) | 13.348(1) |
| $b$, Å | 16.228(6) | 41.145(6) | 13.962(2) |
| $c$, Å | 9.338(2) | 10.352(4) | 12.275(2) |
| $\alpha$, deg | 96.33(2) | 90 | 93.97(1) |
| $\beta$, deg | 107.34(2) | 90 | 97.55(1) |
| $\gamma$, deg | 73.03(2) | 90 | 97.30(1) |
| $V$, Å$^3$ | 1560.3(8) | 13733(5) | 2240.8(5) |
| $Z$ | 2 | 16 | 2 |
| $\mu$, cm$^{-1}$ | 39.27 | 37.47 | 66.18 |
| $\rho$, g cm$^{-3}$ | 1.648 | 1.644 | 1.954 |
| $R^c$ | 0.035 | 0.037 | 0.053 |
| $R_w{}^c$ | 0.083 | 0.092 | 0.167 |
| CCDC | 276911 | 276912 | 276913 |

[a] As chloroform hemisolvate. [b] As dichloromethane hemisolvate. [c] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ for data with $I > 2\sigma(I)$; $R_w(F) = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$ for all data.

**$Tp^*WS(S_2PPh_2\text{-}S)(CO)$.** A suspension of $Tp^*W(S_2PPh_2)(\kappa^2\text{-}MeCN)(CO)$ (0.80 g, 1.03 mmol) in 1:1 acetonitrile/tetrahydrofuran (30 mL) was heated to 75 °C and propylene sulfide (0.15 mL, 1.92 mmol) added. The reaction mixture was heated for 7 h and then reduced to dryness. The residue was column chromatographed on silica gel using 2:1 dichloromethane/hexane and the green fraction collected. The product was recrystallized from dichloromethane/methanol to give green crystals of the dichloromethane hemisolvate (detected by microanalysis and NMR) that were filtered, washed with methanol (5 mL), and dried in vacuo. Yield: 0.45 g, 57%.

Anal. Calcd for $C_{28.5}H_{33}BClN_6OPS_3W$: C, 41.10; H, 3.99; N, 10.09; S, 11.55. Found: C, 41.14; H, 4.01; N, 10.11; S, 11.58. IR (KBr, cm$^{-1}$): $\nu$(BH) 2551, $\nu$(CN) 1542, $\nu$(P=S) 652, $\nu$(PS) 536 (also see Table 1).

**$Tp^*WS\{S_2PR^*{}_2\text{-}S\}(CO)$ ($R^* = (-)$-Mentholate).** A solution of $Tp^*W\{S_2PR^*{}_2\}(\kappa^2\text{-}MeCN)(CO)$ (0.82 g, 0.86 mmol) in 1:1 acetonitrile/tetrahydrofuran (40 mL) and propylene sulfide (0.15 mL, 1.92 mmol) was heated at 75 °C for 10 h. The mixture was reduced to dryness, and the residue was column-chromatographed (twice) on silica gel using 1:1 dichloromethane/hexane as the eluent. Separate green fractions (D1 and D2) were collected. The products were recrystallized from dichloromethane/methanol to give green crystals that were filtered, washed with methanol (5 mL), and dried in vacuo. Yield: D1 = 0.20 g; D2 = 0.23 g. Total yield: 0.43 g, 53%.

Anal. Calcd for $C_{36}H_{60}BN_6O_3PS_3W$: C, 45.67; H, 6.39; N, 8.88; S, 10.16. Found: C, 45.76; H, 6.43; N, 8.95; S, 10.20. IR (KBr, cm$^{-1}$): D1, $\nu$(BH) 2557, $\nu$(CN) 1544, $\nu(PO_{alkyl})$ 932, 974, $\nu$(P=S) 666, $\nu$(PS) 565; D2, $\nu$(BH) 2553, $\nu$(CN) 1544, $\nu(PO_{alkyl})$ 932, 989, $\nu$(P=S) 661, $\nu$(PS) 569 (also see Table 1).

**$Tp^*WI(CO)(\mu\text{-}O)WOITp^*$.** A solution of $Tp^*WOI(CO)$ (1.0 g, 1.53 mmol) in dried, deoxygenated toluene (35 mL) was refluxed for 2 h. The reaction mixture was then reduced to dryness, and the residue was column-chromatographed on silica gel using 2:1 dichloromethane/hexane as the eluent. The intensely colored purple fraction was collected, and the product was recrystallized from dichloromethane/hexane as green crystals with a metallic luster. These were isolated by filtration, washed with hexane (5 mL), and dried in vacuo. Yield: 0.60 g, 60%. The complex was isolated as the dichloromethane hemisolvate (detected by NMR and microanalysis).

Anal. Calcd for $C_{31.5}H_{45}B_2ClI_2N_{12}O_3W_2$: C, 28.70; H, 3.44; N, 12.75. Found: C, 28.84; H, 3.55; N, 12.71. IR (KBr, cm$^{-1}$): $\nu$(BH) 2549, $\nu$(CN) 1544, $\nu_{as}$(WOW) 788, $\nu_s$(WOW) 410 (also see Table 1).

**$Tp^*WO\{S_2P(OPr^i)_2\}$.** A solution of $Tp^*WO\{S_2P(OPr^i)_2\}(CO)$ (0.83 g, 1.12 mmol) in tetrahydrofuran (40 mL) was refluxed for 30 min. The reaction mixture was then reduced to dryness, the residue was column-chromatographed on silica gel/dichloromethane, and the violet fraction was collected. The product was recrystallized from dichloromethane/hexane to give violet crystals that were filtered, washed with hexane (5 mL), and dried in vacuo. Yield: 0.49 g, 62%.

Anal. Calcd for $C_{21}H_{36}BN_6O_3PS_2W$: C, 35.51; H, 5.11; N, 11.83; S, 9.03. Found: C, 35.57; H, 5.07; N, 11.72; S, 9.11. IR (KBr, cm$^{-1}$): $\nu$(BH) 2545, $\nu$(CN) 1543, $\nu$(W=O) 943 (also see Table 1).

**Crystallography.** Dark-pink crystals of $Tp^*WO(S_2PPh_2)(CO)$ and pale-green crystals of $Tp^*WS(S_2PPh_2)(CO)\cdot 0.5CHCl_3$ were grown by slow diffusion of methanol into saturated dichloromethane and chloroform solutions, respectively, of the complexes. Metallic-green crystals of $Tp^*WI(CO)(\mu\text{-}O)WOITp^*\cdot 0.5CH_2Cl_2$ were grown aerobically by slow diffusion of hexane into a saturated dichloromethane solution of the complex. Intensity data for each compound were measured at room temperature (20 °C) on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo Kα radiation, $\lambda = 0.710\,69$ Å. The $\omega - 2\theta$ scan technique was employed to measure 7536 data for a crystal of $Tp^*WO(S_2PPh_2)(CO)$ with dimensions 0.13 × 0.13 × 0.34 mm$^3$ such that $\theta_{max}$ was 27.5°. For $Tp^*WS(S_2PPh_2)(CO)\cdot 0.5CHCl_3$, 3342 data were collected for a crystal of dimensions 0.05 × 0.16 × 0.24 mm$^3$ with $\theta_{max} = 25.0°$, and for $Tp^*WI(CO)(\mu\text{-}O)WOITp^*\cdot 0.5CH_2Cl_2$, 7200 data for a sample 0.07 × 0.18 × 0.21 mm$^3$ were measured so that $\theta_{max}$ was 25.1°. The data sets were corrected for Lorentz and polarization effects,[39] and an empirical absorption correction was applied in each case.[40] Relevant crystal data are given in Table 2.

The structures were each solved by direct methods[41] and refined by a full-matrix least-squares procedure based on $F^2$.[42] Non-H atoms of the complexes were refined with anisotropic displacement parameters, H atoms were included in the models at their calculated positions, and a weighting scheme of the form $w = 1/[\sigma^2(F_o{}^2) +$

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(39) *teXsan: Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1997.

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(41) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389−393.

(42) Sheldrick, G. M. *SHELXL-97 Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

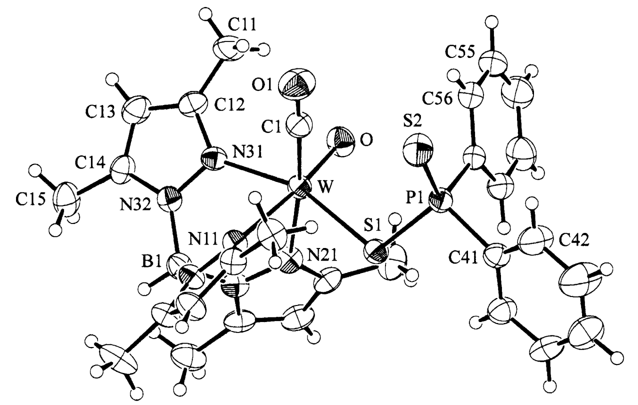

**Figure 1.** Molecular structure of Tp*WO($S_2PPh_2$)(CO). The numbering of the atoms in the pyrazole rings containing N11 and N21 parallels that shown for the ring containing N31.

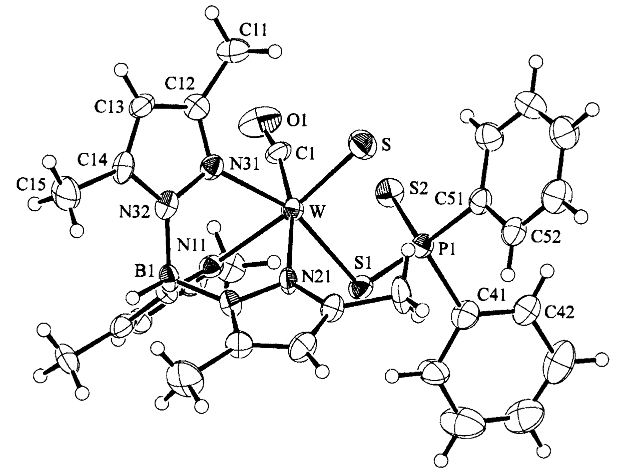

**Figure 2.** Molecular structure of Tp*WS($S_2PPh_2$)(CO). The numbering of the atoms in the pyrazole rings containing N11 and N21 parallels that shown for the ring containing N31.

$(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$, was applied. In the sulfido compound, a disordered chloroform molecule, located about a 2-fold axis, was modeled (ratio of complex to solvent = 2:1) with the use of soft restraints on the C−Cl bond distances and with isotropic thermal parameters; H atoms were not included for this molecule. The nature of the disorder, i.e., the molecule appearing somewhat flattened, may be ascribed to the nature of the intermolecular contacts involving the chloroform molecule and consequent steric crowding (see the Results and Discussion section). In the structure of the dinuclear complex, a partially occupied dichloromethane molecule (ratio of complex to solvent = 2:1) was located and treated as above but with the inclusion of H atoms. The absolute structure of the sulfido compound was confirmed by the value of the Flack parameter, i.e., −0.001(13).[43] Final refinement details are collected in Table 2, and the numbering schemes employed are shown in Figures 1−3, drawn with ORTEP[44] at the 35% probability level.

## Results and Discussion

**Synthesis and Characterization.** The dicarbonyl complexes Tp*WX$(CO)_2$ (X = Cl, Br, I)[35,36] react with dioxygen at room temperature in tetrahydrofuran to produce carbonyloxotungsten(IV) complexes, Tp*WOX(CO). The reactions (eq 1) are accompanied by the generation of carbon dioxide, with the reaction times following the order Cl < Br < I. No intermediates in the reactions were detectable by conventional IR spectroscopy. The complexes could be similarly prepared from the tricarbonyl complexes, Tp*WX$(CO)_3$.[35,36] The literature syntheses of the iodo and bromo derivatives[25] were optimized for higher yield and purity, while Tp*WOCl(CO) is reported here for the first time.

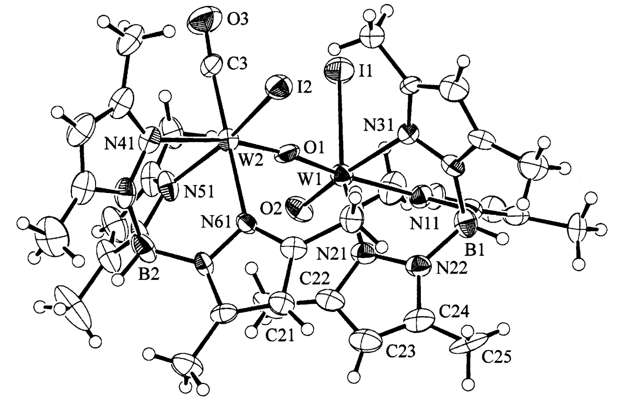

**Figure 3.** Molecular structure of Tp*WI(CO)(μ-O)WOITp*. The numbering of the atoms in the pyrazole rings containing N11 and N31−N61 parallels that shown for the ring containing N21.

$$\mathrm{Tp^*WX(CO)_2 + O_2 \rightarrow Tp^*WOX(CO) + CO_2}\uparrow \qquad (1)$$

The mechanism of the reaction is proposed to involve coordination of dioxygen, followed by nucleophilic attack on a carbonyl ligand to give an $\eta^2$-peroxycarbonyl (or peroxyformate) intermediate, Tp*WX{$\eta^2$-C(O)$O_2$}(CO) (although intermolecular processes producing bridging peroxycarbonyl species[45] cannot be excluded). The peroxycarbonyl species may undergo direct O−O bond cleavage to yield product or rearrangement, to form an $\eta^2$-carbonate species, followed by O−C bond scission, with the same net result. Peroxycarbonyl intermediates have been proposed to form in a number of metal carbonyl autoxidations, leading to metal carbonates and/or $CO_2$. For example, *trans*-Os(NO){$\eta^2$-C(O)-$O_2$}Cl$(PPh_3)_2$, the initial product of the reaction of *trans*-Os(NO)Cl(CO)$(PPh_3)_2$ with dioxygen, rearranges to produce *trans*-Os(NO)($\eta^2$-$CO_3$)Cl$(PPh_3)_2$ and reacts with $PPh_3$ (and other phosphines) to give Os(NO)Cl$(PPh_3)_3$ (and related complexes), $CO_2$, and phosphine oxides.[46−48] The formulation of the peroxycarbonyl complex was recently confirmed by X-ray crystallography.[47] A peroxycarbonyl intermediate has also been postulated to form during the autoxidation of ($Pr_3$tcn)W(NO)(CO)$(CH_3)$ ($Pr_3$tcn = 1,4,7-triisopropyl-1,4,7-triazacyclononane), a reaction that produces ($Pr_3$tcn)W(NO)-(O)$(CH_3)$.[49] The formation of a dioxygen-bridged dimer,

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$[Tp^*WX(CO)]_2(\mu\text{-}O_2)$, followed by homolytic cleavage is not consistent with the observation of byproduct $CO_2$.

The complexes are highly soluble in chlorinated solvents and tetrahydrofuran but insoluble in hydrocarbons, alcohols, and acetonitrile. They are air-stable in the solid state but decompose over a period of days in aerobic solutions. The preparation of $Tp^*WOCl(CO)$ in chlorinated solvents leads to formal chlorine atom abstraction from the solvent and low yields of $Tp^*WOCl_2$.[50,51] The complexes undergo thermal decarbonylation, forming dinuclear species, e.g., $Tp^*WI(CO)(\mu\text{-}O)WOITp^*$ (vide infra).

The reactions of 1 equiv of pyridine *N*-oxide with $Tp^*W(S_2PR_2)(CO)_2$ at 0 °C produce $Tp^*WO(S_2PR_2)(CO)$ ($R = OPr^i$, Ph). The pink, diamagnetic complexes are soluble in chlorinated solvents and tetrahydrofuran but insoluble in hydrocarbons, alcohols, and acetonitrile. The complexes undergo thermal decarbonylation to form $Tp^*WO(S_2PR_2)$.[52] Only $Tp^*WO(S_2PPh_2)(CO)$ is stable at room temperature in the solid-state and solution phases.

Sulfur atom transfer (SAT) from propylene sulfide to $Tp^*WX(\kappa^2\text{-}MeCN)(CO)$ produces carbonylsulfidotungsten(IV) species, $Tp^*WSX(CO)$. For the halo complexes, the reaction times are in the order I < Br < Cl; the low yields of $Tp^*WSCl(CO)$ are ascribed to the comparable rates of formation and subsequent (ill-defined) reactions of the complex. These complexes are not accessible via SAT to $Tp^*WX(CO)_x$, with $[Tp^*W(CO)_2]_2(\mu\text{-}S)$ being the major product of these reactions.[53] SAT has been employed in the synthesis of a number of mononuclear sulfidomolybdenum[54−56] and -tungsten[52,57] complexes. It is likely that the reactions of $Tp^*WX(\kappa^2\text{-}MeCN)(CO)$ with propylene sulfide proceed via displacement of the labile nitrile ligand[37] by propylene sulfide, followed by the elimination of propene.

The halo complexes are brown in the solid state but dissolve to give green-brown ($X = Cl$, Br) or orange-brown ($X = I$) solutions; the dithiophosphinate complexes are green in both phases. The air-stable, diamagnetic species are soluble in chlorinated solvents and tetrahydrofuran but insoluble in hydrocarbons and alcohols.

The solid-state IR spectra of the complexes reveal bands characteristic of terminal chalcogenide, carbonyl, and Tp* ligands. The solution spectra of the oxo and sulfido complexes exhibit a single $\nu(CO)$ band in the regions 1995−1965 and 1970−1937 $cm^{-1}$, respectively. The data indicate a greater degree of $E \rightarrow W$ $\pi$ donation and $W \rightarrow CO$ $\pi$ back-bonding for the sulfido complexes compared to the oxo complexes. Similar results have been reported for $WECl_2(CO)(PMePh_2)_2$, where the $\nu(CO)$ bands are observed at 2006 $cm^{-1}$ ($E = O$) and 1986 $cm^{-1}$ ($E = S$).[18−20] Medium-intensity $\nu(W{=}E)$ bands are observed at ca. 955 and 505 $cm^{-1}$, respectively.

The $^1H$ NMR spectra of the complexes are indicative of molecular $C_1$ symmetry with six methyl resonances and three methine resonances from the Tp* ligand. The diastereotopic nature of the dithiophosphate methyl and methylene protons of $Tp^*WO\{S_2P(OPr^i)_2\}(CO)$ and $Tp^*WS\{S_2P(OEt)_2\}(CO)$, respectively, are reflected in the observed resonance patterns. Diastereomeric $Tp^*WS\{S_2P(O\text{-}(-)\text{-menthyl})_2\}(CO)$ exhibits discrete doublet of quartet resonances, each integrating for one proton at $\delta$ 4.31 and 4.44 for D1 and at $\delta$ 4.36 and 4.48 for D2; these are assigned to the $-O-CH$ protons, with the observed multiplicity arising from $^3J_{HH}$ and $^3J_{PH}$ coupling.

$^{13}C\{^1H\}$ NMR spectra exhibit six methyl resonances ($\delta$ 10−20), three pyrazole 4-methine resonances ($\delta$ 107−110) and six pyrazole 3- and 5-methine resonances ($\delta$ 144−156) for the Tp* ligand. Carbonyl ligand resonances are observed in the ranges $\delta$ 274−287 ($J_{WC} = 189{-}196$ Hz) and $\delta$ 272−282 ($J_{WC} = 160{-}165$ Hz) for the oxo and sulfido complexes, respectively. These are significantly deshielded compared to the carbonyl resonance of $WOCl_2(CO)(PMePh_2)_2$ at $\delta$ 234.4.[18,20] The $^{31}P$ resonances of the oxo complexes are shielded relative to the signals of their sulfido analogues, as previously observed for $Tp^*MoE(S_2PR_2)$[58] and $Tp'MoE(S_2PR_2)$ [$Tp'$ = hydro(5-isopropylpyrazolyl)bis(3-isopropylpyrazolyl)borate].[55]

The low-energy bands in the UV−vis spectra of the complexes are assigned to d−d transitions. Similarly, single bands observed in the electronic spectra of $WECl_2(CO)(PMePh_2)_2$ ($E = O$, red-purple; $E = S$, green) were assigned to the $d_{xy} \rightarrow d_{xz}/d_{yz}$ ($n \rightarrow \pi^*$) transition. A lower energy transition was also observed for $WSCl_2(CO)(PMePh_2)_2$ (696 nm) compared to $WOCl_2(CO)(PMePh_2)_2$ (498 nm).[20] The two d−d transitions observed imply the nondegeneracy of the $d_{xz}$ and $d_{yz}$ orbitals. The bonding in carbonyloxo and carbonylsulfido complexes has been discussed; only the cis conformation provides the orbital overlap necessary for the simultaneous stabilization of the $\pi$-base and $\pi$-acid ligands.[20,23]

### Synthesis and Characterization of $Tp^*WI(CO)(\mu\text{-}O)WOITp^*$

Thermal decarbonylation of $Tp^*WOI(CO)$ in toluene results in the formation of dark-purple $Tp^*WI(CO)(\mu\text{-}O)WOITp^*$ (eq 2). The mechanism of the reaction is likely to involve decarbonylation of $Tp^*WOI(CO)$ and attack of unsaturated "Tp*WOI" by a second $Tp^*WOI(CO)$ molecule. The complex is soluble in chlorinated solvents, tetrahydrofuran, and aromatic hydrocarbons and insoluble in alcohols and aliphatic hydrocarbons.

$$2Tp^*WOI(CO) \rightarrow Tp^*WI(CO)(\mu\text{-}O)WOITp^* + CO(g) \quad (2)$$

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The IR spectrum of the complex exhibits bands attributable to the carbonyl [$\nu$(CO) 1870 cm$^{-1}$], terminal oxo [$\nu$(W=O) 962 cm$^{-1}$], $\mu$-oxo [$\nu_{as}$(WOW) 788 cm$^{-1}$], and Tp* ligands. The $\nu$(CO) band is close in energy to the corresponding band in the W$^{III}$ complex Tp*WI$_2$(CO) [$\nu$(CO) = 1876 cm$^{-1}$].[59] The $\nu_{as}$(WOW) band is in the range typical of related species, e.g., Tp*WO$_2$($\mu$-O)WO(CO)Tp* (820 cm$^{-1}$),[24] Tp*MoO$_2$($\mu$-O)MoOClTp* (750 cm$^{-1}$),[60] and [WO(O$_2$R)(HO$_2$R)]$_2$($\mu$-O) (O$_2$R = cyclic 1,2-diolate, 762−791 cm$^{-1}$).[61]

The $^1$H NMR spectrum of the complex exhibits 12 methyl resonances and 6 methine resonances, consistent with molecular $C_1$ symmetry. The $^{13}$C{$^1$H} NMR spectrum of the complex also displays a resonance pattern indicative of molecular $C_1$ symmetry (Table S1 in the Supporting Information). A resonance at $\delta$ 219.8 is assigned to the carbonyl carbon ($J_{WC}$ not observed).

The electronic spectrum of Tp*WI(CO)($\mu$-O)WOITp* is dominated by an intense band at 520 nm ($\epsilon$ = 28 500 M$^{-1}$ cm$^{-1}$). The energy and intensity of this band are typical of the WOW chromophore, as observed in related complexes, including [{WCl$_5$}$_2$($\mu$-O)]$^{4-}$ (535 nm; $\epsilon$ = 19 000 M$^{-1}$ cm$^{-1}$)[32] and [Cp$_2$W(Me)]$_2$($\mu$-O) (525 nm; $\epsilon$ = 23 600 M$^{-1}$ cm$^{-1}$).[62] Molecular orbital treatments have been reported for the electronic structures of the MOM fragment;[34,62] the diamagnetism of these complexes can be explained in terms of spin pairing through $\pi$ interactions within the WOW fragment, a feature invoked to explain the diamagnetism of dinuclear, d$^1$−d$^1$, $\mu$-oxo complexes.[34] The spectroscopic properties and metrical data (vide infra) of the complex are consistent with the presence of a W$^{III}$/W$^{V}$ mixed-valence species, possessing a filled, delocalized three-center (W−O−W) $\pi$ bond and a localized (on W$^{III}$), filled d$_\pi$ orbital that back-bonds to the carbonyl ligand. A detailed description of the bonding in the complex must await further spectroscopic and computational studies.

Decarbonylation of Tp*WO{S$_2$P(OPr$^i$)$_2$}(CO) produces good yields of violet, air-stable, diamagnetic Tp*WO{S$_2$P(OPr$^i$)$_2$}, which is soluble in chlorinated solvents, tetrahydrofuran, aromatic hydrocarbons, acetonitrile, and ether but insoluble in alcohols and aliphatic hydrocarbons. The reactions of Tp*WS(S$_2$PR$_2$)(CO) (R = OEt, Ph) with pyridine *N*-oxide result in the formation of oxosulfido complexes, Tp*WOS(S$_2$PR$_2$), as described elsewhere.[52,63]

**Table 3.** Selected Bond Distances (Å) and Bond Angles (deg) for Tp*WE(S$_2$PPh$_2$)(CO)

| | E = O | E = S |
|---|---|---|
| W−E | 1.698(4) | 2.135(4) |
| W−S1 | 2.4545(15) | 2.448(3) |
| W−N11 | 2.286(4) | 2.281(10) |
| W−N21 | 2.198(4) | 2.199(9) |
| W−N31 | 2.170(4) | 2.188(9) |
| W−C1 | 2.005(5) | 2.012(12) |
| P1−S1 | 2.0631(18) | 2.063(4) |
| P1−S2 | 1.9488(19) | 1.961(4) |
| C1−O1 | 1.145(6) | 1.099(15) |
| E−W−S1 | 102.48(14) | 99.79(14) |
| E−W−N11 | 173.65(16) | 171.4(3) |
| E−W−N21 | 95.60(17) | 102.7(2) |
| E−W−N31 | 94.78(17) | 96.9(3) |
| E−W−C1 | 91.3(2) | 89.2(4) |
| S1−W−N11 | 83.83(11) | 84.9(3) |
| S1−W−N21 | 84.77(11) | 84.0(2) |
| S1−W−N31 | 159.93(11) | 161.4(3) |
| S1−W−C1 | 96.55(16) | 97.5(4) |
| N11−W−N21 | 84.23(15) | 84.9(3) |
| N11−W−N31 | 78.89(15) | 79.6(4) |
| N21−W−N31 | 83.41(15) | 84.3(3) |
| N11−W−C1 | 88.59(18) | 83.1(4) |
| N21−W−C1 | 172.52(18) | 167.7(4) |
| N31−W−C1 | 93.18(18) | 90.9(4) |
| W−S1−P1 | 110.43(7) | 112.51(15) |
| W−C1−O1 | 171.2(5) | 167.8(13) |
| S1−P1−S2 | 119.21(9) | 120.1(2) |

**Crystal Structures.** The molecular structure of Tp*WO(S$_2$PPh$_2$)(CO) is shown in Figure 1, and selected distances and angles are collected in Table 3. The molecule contains a six-coordinate, distorted octahedral tungsten center coordinated by a *fac* tridentate Tp* ligand and mutually cis, oxo, carbonyl, and monodentate diphenyldithiophosphinate ligands. The greatest angular distortions from ideal octahedral geometry are the acute N−W−N bond angles [78.89(15)−84.23(15)°] and an S1−W−N31 angle of 159.93(11)° (vs the ideal angle of 180°). The O−W−S1 angle of 102.48(14)° also deviates from the ideal octahedral angle of 90°. The W=O bond distance of 1.698(4) Å is indicative of a multiple bond and is close to the mean distance for known monooxotungsten(IV) species,[64] comparing well with the W=O bond distance of 1.689(6) Å in WOCl$_2$(CO)(PMePh$_2$)$_2$.[19,20] The carbonyl ligand is nearly perpendicular to the oxotungsten moiety, with ∠(O−W−C1) = 91.3(2)° [cf. 89.6(3)° in WOCl$_2$(CO)(PMePh$_2$)$_2$]. A slight bend in the carbonyl ligand [∠(W−C1−O1) = 171.2(5)°] indicates steric crowding by the terminal sulfur atom of the diphenyldithiophosphinate ligand and/or a partial interaction between the S2 and C1 atoms;[65] the W···S2 separation is >4.0 Å. The W−S1 bond length of 2.4545(15) Å is indicative of a W−S single bond[64] and precludes significant $\pi$ interactions. The W−S1−P1 angle of 110.43(7)° approximates the tetrahedral angle, consistent with sp$^3$ hybridization of S1. The P−S bonds of the dithiophosphinate ligand approximate those found in the free acid, HSP(S)Ph$_2$ [$d$(P−S) = 2.077(1) Å; $d$(P=S) = 1.954(1) Å[66]]. Finally, the W−N11 bond trans to the oxo ligand is ca. 0.1 Å longer than the other two W−N bonds because of the trans influence of the oxo ligand.

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(59) We have prepared this complex from the reaction of Tp*WI(CO)$_2$ with iodine. The paramagnetic complex ($\mu$ = 1.79) exhibits a contact-shifted NMR spectrum and an IR spectrum containing bands typical of Tp* and a $\nu$(CO) band at 1876 cm$^{-1}$. X-ray diffraction has shown the complex to be mononuclear, but the iodo and carbonyl ligands were disordered.

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In the lattice, molecules are linked into discernible chains aligned along the *a* axis via $C23{-}H\cdots S2^{i}$ interactions so that $H\cdots S2^{i}$ is 2.87 Å, $C23\cdots S2^{i}$ is 3.743(7) Å, and the angle at H is 156° (symmetry operation i: $-1 + x, y, z$).

Structurally characterized examples of monomeric organometallic oxotungsten(IV) complexes remain relatively rare.[6] The crystal structure of $Tp^{*}WO(S_2PPh_2)(CO)$ is only the second example of a nondisordered, mononuclear carbonyloxo complex, with the other being $WOCl_2(CO)(PMePh_2)_2$.[19,20]

The molecular structure of $Tp^{*}WS(S_2PPh_2)(CO)$ is shown in Figure 2, and selected distances and angles are collected in Table 3. The structure is analogous to that of $Tp^{*}WO(S_2PPh_2)(CO)$ but with a terminal sulfido ligand in place of the oxo ligand. The greatest distortions from ideal octahedral geometry are similar to those detailed above for $Tp^{*}WO(S_2PPh_2)(CO)$; see Table 3. The structure of $Tp^{*}WS(S_2PPh_2)(CO)$ is the first reported for a monomeric carbonylsulfido complex of any metal.

The W−S1 bond distance of 2.135(4) Å is indicative of a W−S multiple bond.[64] This is in agreement with the W═S distances observed for other mononuclear sulfidotungsten(IV) complexes, e.g., $WS(\eta^2\text{-}PhC_2Ph)(S_2CNEt_2)_2$,[67] $WS(\eta^2\text{-}PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$,[68] $WS(S_2CNEt_2)(\eta^4\text{-}C_4Ph_4H)$,[69] $Tp^{*}WS(S_2CNEt_2)$,[57] and $Tp^{*}WS(S_2PPh_2)$[52] [in the range 2.103(4)−2.153(2) Å]. The carbonyl ligand lies perpendicular to the W−S bond axis [$\angle$(S−W−C1) 89.2(4)°]. The carbonyl ligand is bent [$\angle$(W−C1−O1) = 167.8(13)°], and the thiophosphinate S2 atom is proximal to the C1 atom of the carbonyl ligand as described above. The W−S1 bond length of 2.448(3) Å is indicative of a W−S single bond.[64] The W−S1−P1 bond angle of 112.51(15)° approximates the tetrahedral angle for S1. The W−N11 bond distance trans to the sulfido ligand is the longest, consistent with the trans influence of the sulfido ligand.

The face-centered orthorhombic lattice of $Tp^{*}WS(S_2PPh_2)(CO)\cdot 0.5CHCl_3$ comprises 16 molecules of the complex as well as 8 disordered (about a 2-fold axis) chloroform molecules. The closest non-H contacts of 3.024(11) Å involve the Cl1 atom, lying on a 2-fold axis, and a pair of carbonyl O1 atoms (symmetry operations: $x, -\frac{1}{2} + y, -\frac{1}{2} + z$ and $\frac{1}{2} - x, -y, -\frac{1}{2} + z$). In this way, complex molecules are associated into pairs about a 2-fold axis mediated by the chloroform molecules.

**Table 4.** Selected Bond Distances (Å) and Bond Angles (deg) for $Tp^{*}WI(CO)(\mu\text{-}O)WOITp^{*}$.

| | | | |
|---|---|---|---|
| W1−O1 | 1.910(10) | W2−I2 | 2.7593(13) |
| W1−O2 | 1.719(10) | W2−C3 | 1.928(17) |
| W1−I1 | 2.7605(14) | W2−N41 | 2.199(13) |
| W1−N11 | 2.186(13) | W2−N51 | 2.160(13) |
| W1−N21 | 2.126(13) | W2−N61 | 2.245(12) |
| W1−N31 | 2.317(12) | C3−O3 | 1.133(19) |
| W2−O1 | 1.871(10) | | |
| O1−W1−O2 | 102.1(5) | O1−W2−C3 | 92.3(5) |
| O1−W1−I1 | 94.7(3) | O1−W2−I2 | 106.6(3) |
| O1−W1−N11 | 164.6(5) | O1−W2−N41 | 167.6(5) |
| O1−W1−N21 | 94.1(4) | O1−W2−N51 | 90.2(5) |
| O1−W1−N31 | 84.3(4) | O1−W2−N61 | 91.1(4) |
| O2−W1−I1 | 93.8(4) | C3−W2−I2 | 89.7(5) |
| O2−W1−N11 | 92.5(5) | C3−W2−N41 | 93.0(6) |
| O2−W1−N21 | 93.5(5) | C3−W2−N51 | 94.9(6) |
| O2−W1−N31 | 173.5(5) | C3−W2−N61 | 175.5(6) |
| I1−W1−N11 | 89.3(3) | I2−W2−N41 | 84.6(3) |
| I1−W1−N21 | 167.1(4) | I2−W2−N51 | 162.4(3) |
| I1−W1−N31 | 86.9(3) | I2−W2−N61 | 86.4(3) |
| N11−W1−N21 | 79.8(5) | N41−W2−N51 | 78.2(5) |
| N11−W1−N31 | 81.0(4) | N41−W2−N61 | 84.4(5) |
| N21−W1−N31 | 84.7(5) | N51−W2−N61 | 88.1(5) |
| W1−O1−W2 | 173.1(6) | W2−C3−O3 | 175.5(16) |

The molecular structure of $Tp^{*}WI(CO)(\mu\text{-}O)WOITp^{*}$ is shown in Figure 3, and selected bond distances and angles are presented in Table 4. The dinuclear complex comprises two six-coordinate, distorted octahedral tungsten centers linked by a single oxo ligand; the bridge is characterized by W1−O1 and W2−O1 distances of 1.910(10) and 1.871(10) Å, respectively, and a near-linear W1−O1−W2 angle of 173.1(6)°. The coordination sphere of W1 is completed by carbonyl, iodo, and tridentate *fac* Tp* ligands, while oxo, iodo, and tridentate *fac* Tp* ligands coordinate to W2. The carbonyl and iodide ligands on adjacent W atoms are syn and the oxo and iodide ligands anti; this arrangement is consistent with molecular $C_1$ symmetry. The W1−I1 and W2−I2 distances of 2.7605(14) and 2.7593(13) Å, respectively, are experimentally equivalent and compare well with values reported for $[CpMoOI]_2(\mu\text{-}O)$ [2.709(1) Å].[70] The W−N bond trans to O2 was elongated by just over 0.1 Å compared to the other W−N bonds.

A number of dinuclear oxo-bridged W complexes have been structurally characterized. The geometry at the bridging oxygen varies considerably, from bent in $(tcn)WO_2(\mu\text{-}O)WO(O_2)_2(H_2O)$ (tcn = 1,4,7-triazacyclononane) [152.2(2)°][71] and $[W(O)(chpd)(Hchpd)]_2(\mu\text{-}O)$ (chpd = *trans*-cycloheptane-1,2-diol) [154.3(9)°][61] to linear in $[Cp_2W(Me)]_2(\mu\text{-}O)$,[62] $[\{WO_2(citrate)\}_2(\mu\text{-}O)]^{6-}$,[72] and $[WO(CH_2CMe_3)_3]_2(\mu\text{-}O)$.[73] Intermediate degrees of bending are observed in $Tp^{*}WO_2(\mu\text{-}O)WO(CO)Tp^{*}$ [169.2(2)°][24] and the molybdenum complexes $[Tp^{*}MoO_2]_2(\mu\text{-}O)$ [167.1(2)°][74] and $[(HBpz_3)MoOCl]_2(\mu\text{-}O)$ [177.3(2)°].[75] Metal-bridging oxo bond distances in complexes of this type range from 1.829(4) to 1.977(10) Å.

The dinuclear complex crystallizes as the dichloromethane hemisolvate. The dichloromethane molecule is positioned so as to bridge two methyl−H atoms of the Tp* ligand bound to the W1 atom via $C1\cdots H$ contacts, i.e., $C35{-}H\cdots Cl1$ is 3.14 Å and $C25{-}H\cdots Cl2$ is 2.96 Å (symmetry operation: $1 - x, 1 - y, 1 - z$). Additionally, the dichloromethane

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molecule bridges, again via Cl⋯H interactions (C55−H⋯Cl1 is 3.15 Å for symmetry operation 1 − *x*, −*y*, −*z*), symmetry-related complexes thereby providing links that form a chain motif aligned along the *bc* diagonal.

**Summary.** A range of new carbonyloxo and carbonylsulfidotungsten(IV) complexes have been prepared and characterized. The controlled oxidation of carbonyl precursors, leading to very stable mononuclear carbonyl chalcogenide complexes, is a notable aspect of the work described. The cis structures and properties of the complexes can be rationalized in terms of optimal $\pi$-orbital overlap between the metal d and the $\pi$-donor and $\pi$-acceptor orbitals of the ligands. A unique $W^{III}/W^{V}$ mixed-valence complex is produced upon decarbonylation of Tp*WOI(CO).

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**Supporting Information Available:** A table of $^{13}$C NMR data (Table S1) and details of the X-ray crystal structures (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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