Reactivity and crystal structures of the first dithiocarbamate chromium(0) and dithiophosphate tungsten(0) complexes: crystal structures of [Et$_4$N][Cr(η^2-S$_2$CNC$_5$H$_{10}$)(CO)$_4$] and [Et$_4$N][W{η^2-S$_2$P(OEt)$_2$(CO)$_4$]

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Abstract

The structures of first dithiocarbamate chromium(0) complex [Et$_4$N][Cr(η^2-S$_2$CNC$_5$H$_{10}$)(CO)$_4$] (**1**) and the diethyldithiophosphate tungsten(0) complex [Et$_4$N][W{η^2-S$_2$P(OEt)$_2$(CO)$_4$] (**2**) have been determined by X-ray diffraction analyses. Crystal data for **1**: space group, $P2_1$ with $a = 10.240(2)$ Å, $b = 12.705(4)$ Å, $c = 9.888(2)$ Å, $\beta = 117.26(2)°$, $V = 1143.6(4)$ Å^3, and $Z = 2$. The structure was refined to $R = 0.027$ and $R_w = 0.028$; Crystal data for **2**: space group, $C2/c$ with $a = 13.054(6)$ Å, $b = 16.220(4)$ Å, $c = 11.417(3)$ Å, $\beta = 93.73(3)°$, $V = 2412.3(14)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.026$ and $R_w = 0.019$. The geometry around the metal atom in the anion of these two complexes is a distorted octahedron. The dithiocarbamato and diethyldithiophosphato ligands, respectively, coordinate to the Cr and W metal center through the two sulfur atoms. The short C–N bond length of 1.335(4) Å in **1** indicates a considerable partial double bond character. The allyl dithiophosphate tungsten complex [W(CH$_3$CN)(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$}] (**3**) can be obtained from the reaction of [W(CH$_3$CN)$_2$(η^3-C$_3$H$_5$)(CO)$_2$Br] and (EtO)$_2$PS$_2$NH$_4$ in CH$_3$CN at room temperature but decomposed in the reaction of **2** with allyl bromide. Complex **3** reacted with dppe in CH$_2$Cl$_2$ at room temperature to give a mixture of complex [W(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$}]$_2$(μ-dppe) (**4**) and [W(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$(η^1-dppe)] (**5**).
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1. Introduction

Although the chemistry of dithio–metal complexes have been widely studied in bonding mode [1], cubane-like cluster [2], bisalkyne complexes [3], catalyst [4], and redox-active enzymes [5], only very few dithio-M(VIB)(0) derivatives have been reported so far.

A recent article reported the synthesis of dithiocarbamate metal complexes of the type [Et$_4$N][M(η^2-S$_2$CNEt$_2$)(CO)$_4$] (M = Mo, W) [6] from the direct reaction of M(CO)$_6$ with NaS$_2$CNEt$_2$ in the presence of Et$_4$NCl in MeCN but the analogue chromium complex could not be synthesized by this method. The late transition-metal dithiophosphato complexes are most common, while the early transition metals are quite rare. For the VIB group, complexes involving dithiophosphato ligands have been reported in high oxidation-state [7]. The low oxidation-state of the organometallic dithiophosphate molybdenum complexes have been studied in [Et$_4$N][Mo{η^2-S$_2$P(OEt)$_2$(CO)$_4$]] [8], [CpMo{η^2-S$_2$P(OR)$_2$}$_2$(NO)] [9], [Mo{η^2-S$_2$P(OEt)$_2$}(CO)$_2$(S$_2$CPCy$_3$)(SnPhCl$_2$)] [10] and [Mo(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$}]$_2$(μ-NH$_2$NH$_2$) [11]. Some reports described the [Cat][M(CO)$_4$L–L] (Cat = Na, K, NH$_4$; L–L = dithiocarbamato, xanthato, dithiophosphato) type complexes and these complexes were very unstable and non-isolable [12]. Notably, till now,

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these complexes are rarely subjected to crystallographic study [13] and there is no example involving the dithiocarbamate Cr(0) or dithiophosphate W(0) complex.

Our interest in the sulfur containing ligands [14] and the paucity of Cr(0) and W(0) complexes involving $R_2NCS_2^-$ or $(EtO)_2PS_2^-$ ligands prompted us to explore the possibility of obtaining the crystal structures of these complexes.

2. Results and discussion

2.1. X-ray structures determination of [Et₄N][Cr(η²-S₂CNC₅H₁₀)(CO)₄] (1) and [Et₄N][W{η²-S₂P(OEt)₂}(CO)₄] (2)

We have reported the reaction of $(pip)_2Cr(CO)_4$ (pip: piperidine, $C_5H_{10}NH$) complexes with n-BuLi and CS_2 in the presence of Et_4NBr to give complex $[Et_4N][Cr(\eta^2\text{-}S_2CNC_5H_{10})(CO)_4]$ (1) [15] and the nucleophilic substitution method in the reaction of $(EtO)_2PS_2NH_4$ with $(pip)_2W(CO)_4$ in refluxing CH_3CN which leads to the formation of the diethyldithiophosphate complex $[Et_4N][W\{\eta^2\text{-}S_2P(OEt)_2\}(CO)_4]$ (2) [8] in the presence of Et_4NBr (Scheme 1).
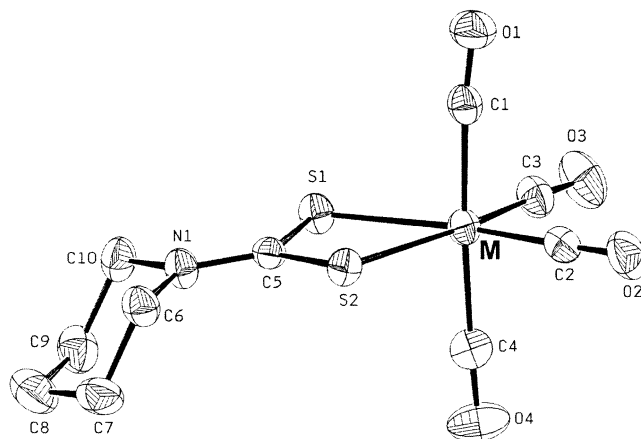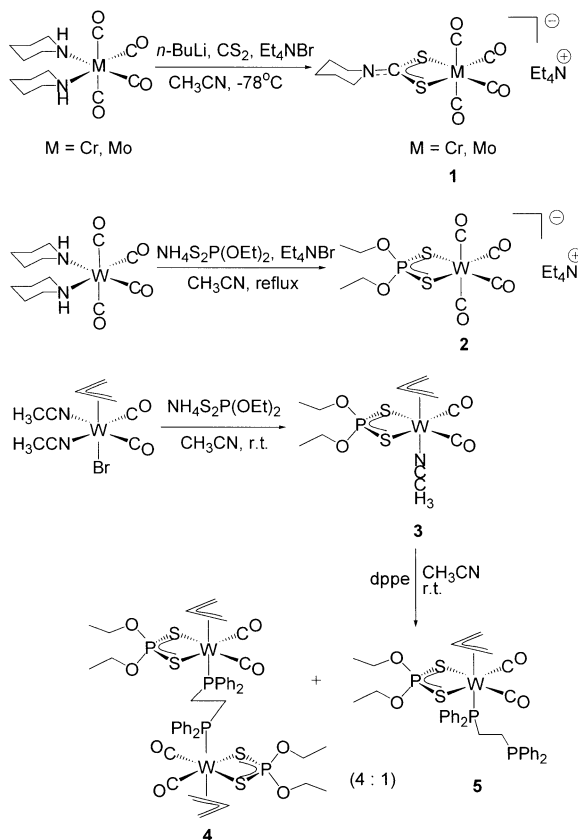

Fig. 1. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the anionic complex $[Et_4N][M(\eta^2\text{-}S_2CNC_5H_{10})(CO)_4]$ (M = Cr, 1; M = Mo).

The ORTEP plots of the anion moiety of 1 and 2 are shown in Figs. 1 and 2, respectively. The cell constants and other pertinent data are shown in Table 1. Tables 2 and 4 contain selected bond distances and angles of 1 and 2, respectively. As shown in the ORTEP plots, the geometry around the metal atom in the anion of the two compounds are both a distorted octahedron with a small SCrS angle of 70.84(5)° and a small dihedral angle of 1.01° between the plane CrS(1)S(2) and the plane CrC(2)C(3) in 1 and a small SWS(a) angle of 76.07(7)° and a small dihedral angle of 0.47° between the plane WSS(a) and the plane WC(4)C(4a) in 2. The dihedral angles in 1 between the plane CrC(1)C(4) and the plane CrS(1)S(2) and between the plane CrC(1)C(4) and the plane CrC(2)C(3) are 89.87 and 89.65°, respectively, and between the plane WC(3)C(3a) and the plane WSS(a) and between the plane WC(3)C(3a) and the plane WC(4)C(4a) are 90.25 and 89.78° in 2, respectively. The anion structure of 1 possesses a pseudo-C_2 axis through Cr, C(5) and N(1) atoms and thus acquires a
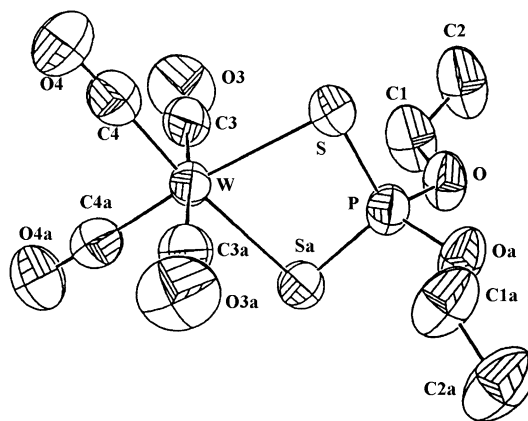

Scheme 1.

Fig. 2. An ORTEP drawing with 30% thermal ellipsoids and atom-numbering scheme for the anionic complex $[Et_4N][W\{\eta^2\text{-}S_2P(OEt)_2\}(CO)_4]$ (2).

Table 1

Crystal data and refinement details for complexes [Et$_4$N][Cr(η^2-S$_2$CNC$_5$H$_{10}$)(CO)$_4$] (1) and [Et$_4$N][W{η^2-S$_2$P(OEt)$_2$}(CO)$_4$] (2)

	1	2
Formula	C$_{18}$H$_{30}$N$_2$O$_4$S$_2$Cr	C$_{16}$H$_{30}$NO$_6$PS$_2$W
Formula weight	454.56	611.35
Crystal system	Monoclinic	Monoclinic
Crystal size (mm)	0.50 × 0.50 × 0.40	0.35 × 0.40 × 0.40
Space group	P2$_1$	C2/c
a (Å)	10.240(2)	13.054(3)
b (Å)	12.705(4)	16.220(3)
c (Å)	9.888(2)	11.416(2)
β (°)	117.260(15)	93.73(2)
V (Å^3)	1143.6(4)	2412.3(8)
Z	2	4
D$_{calc.}$ (g cm^{-3})	1.302	1.683
μ (Mo–K$_\alpha$) (cm^{-1})	6.855	5.056
F(000)	480	1208
2θ$_{max}$	50.0	50.0
h,k,l range	−12→10, 0→15, 0→11	−15→15, 0→19, 0→13
Reflections collected	2110	2124
Obs. data [I > 2σ(I)]	1797	2124
No. of parameters	244	124
R ^{a}	0.027	0.026
Rw ^{b}	0.028	0.063
Transmission (min., max.)	0.900, 1.000	0.205, 0.147
Number of atoms	57	57
Quality-of-fit ^{c}	1.33	1.01
Δ(D-map) max./min. (e Å^{-3})	−0.120; 0.190	−0.489; 0.688

^{a} $R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$.
^{b} $Rw = [\Sigma\omega(|Fo|-|Fc|)^2]^{1/2}$; $\omega = 1/\sigma^2(|Fo|)$.
^{c} Quality-of-fit $= [\Sigma\omega(|Fo|-|Fc|)^2/(N_{reflections}-N_{parameters})]^{1/2}$.

pseudo-C_{2v} symmetry, whereas the anion of **2** possesses a C_2 crystallographic axis through W and P atoms and thus has a molecular symmetry of C_{2v}. Complexes **1** and **2** possess two groups of Cr–CO bond distances (*trans* carbonyl 1.876(4), *cis* carbonyl 1.818(4) Å (average)) and two group of W–CO bond distances of 2.012(6) and 1.927(6) Å. The significantly different bond distances are due to the *trans* influence of the carbonyl groups.

The dithiocarbamato group of **1** exhibits two C–S (1.707(4) and 1.717(4) Å) and one C–N (1.335(4) Å) bond lengths and they are nearly identical with those found in the Mo complex, [Et$_4$N][Mo(η^2-S$_2$CNC$_5$H$_{10}$)(CO)$_4$] [16] (1.705(4), 1.716(4) and 1.336(5) Å) and the W complex, [Et$_4$N][W(η^2-S$_2$CNC$_5$H$_{10}$)(CO)$_4$] (1.708(7), 1.705(7) and 1.335(9) Å) as well as [Et$_4$N][Mo(η^2-S$_2$CNEt$_2$)(CO)$_4$] (1.692(12), 1.719(13) and 1.329(13) Å) [6] complex within the experimental errors. The two Cr–S bond distances (2.4776(13) and 2.4679(12) Å) are significantly shorter than the two Mo–S bond distances (2.5898(16) and 2.5978(13) Å) and the two W–S bond distances (2.6061(21) and 2.5649(22) Å) [8] due to the first row Group VIB metal of the Cr. The short C(5)–N(1) bond

Table 2

Selected bond distances (Å) and angles (°) for 1

Bond lengths

Cr–S(1)	2.4733(13)	C(6)–N(1)	1.458(5)
Cr–S(2)	2.4730(12)	C(7)–C(8)	1.515(8)
Cr–C(1)	1.886(5)	C(8)–C(9)	1.508(8)
Cr–C(2)	1.820(4)	C(9)–C(10)	1.503(7)
Cr–C(3)	1.833(4)	C(10)–N(1)	1.462(5)
Cr–C(4)	1.878(5)	C(1)–O(1)	1.148(6)
S(1)–C(5)	1.707(4)	C(2)–O(2)	1.163(5)
S(2)–C(5)	1.717(4)	C(3)–O(3)	1.152(5)
C(5)–N(1)	1.334(5)	C(4)–O(4)	1.142(6)
C(6)–C(7)	1.498(6)		

Bond angles

S(1)–Cr–S(2)	70.84(4)	S(l)–C(5)–S(2)	113.74(19)
S(1)–Cr–C(1)	93.51(13)	S(1)–C(5)–N(1)	123.3(3)
S(1)–Cr–C(2)	170.77(14)	S(2)–C(5)–N(1)	122.9(3)
S(1)–Cr–C(3)	98.49(14)	C(7)–C(6)–N(1)	110.5(4)
S(1)–Cr–C(4)	89.71(14)	C(6)–C(7)–C(8)	111.7(4)
S(2)–Cr–C(1)	92.73(12)	C(7)–C(8)–C(9)	110.6(4)
S(2)–Cr–C(2)	99.99(14)	C(8)–C(9)–C(10)	111.2(4)
S(2)–Cr–C(3)	169.25(14)	C(9)–C(10)–N(1)	110.6(4)
S(2)–Cr–C(4)	89.44(13)	C(5)–N(1)–C(6)	123.8(3)
C(1)–Cr–C(2)	87.93(18)	C(5)–N(1)–C(10)	122.2(3)
C(1)–Cr–C(3)	89.14(18)	C(6)–N(1)–C(10)	113.5(3)
C(1)–Cr–C(4)	176.57(18)	Cr–S(2)–C(5)	87.44(12)
C(2)–Cr–C(3)	90.65(19)	Cr–C(1)–O(1)	174.4(4)
C(2)–Cr–C(4)	89.09(18)	Cr–C(2)–O(2)	178.2(4)
C(3)–Cr–C(4)	89.21(19)	Cr–C(3)–O(3)	177.2(4)
Cr–S(1)–C(5)	87.65(12)	Cr–C(4)–O(4)	177.6(4)

length of 1.335(4) Å in **1** indicates considerable partial double bond character as is typical for the chelating 1,1-dithiolate ligands [17].

The W–S bond distance of 2.6102(14) Å in **2** is longer than those found in the dithiocarbamate complexes [Et$_4$N][W(η^2-S$_2$CNC$_4$H$_8$)(CO)$_4$] (average value of W–S bonds, 2.590(3) Å) and [Et$_4$N][W(η^2-S$_2$CNC$_5$H$_{10}$)(CO)$_4$] (2.5855(22) Å). It reflects the large π accepting ability of R$_2$NCS$_2^-$ ligand than the (EtO)$_2$PS$_2^-$ ligand. In fact, the (EtO)$_2$PS$_2^-$ ligand can be replaced by the Et$_2$NCS$_2^-$ ligand under some reaction conditions [8]. The SWS(a) angle 76.07(7)° of **2** is similar to the angle 76.5(1)° in the complex [CpMo{η^2-S$_2$P(OEt)$_2$}(CO)$_2$], 77.32(5)° in the complex [Mo(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$}]$_2$(μ-NH$_2$NH$_2$) and 75.87(5)° in the complex [Et$_4$N][Mo{η^2-S$_2$P(OEt)$_2$(CO)$_4$]] [8] which are all within the experimental errors. Other important bond distances and angles of dithiocarbamate and dithiophosphate VIB metal complexes are listed in Table 6.

2.2. Synthesis of complex [W(CH$_3$CN)(η^3-C$_3$H$_5$)(CO)$_2${η^2-S$_2$P(OEt)$_2$}] (3)

In an attempt to synthesize the allyl dithiophosphate W complex as that in Mo system [8], we treated of [Et$_4$N][W{η^2-S$_2$P(OEt)$_2$(CO)$_4$}] (**2**) with allyl bromide in CH$_3$CN at room temperature. However, there was no reaction but decomposed in the refluxing temperature.

However, complex $[W(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ (3) can be obtained from the reaction of $[W(CH_3CN)_2(\eta^3-C_3H_5)(CO)_2Br]$ and $NH_4(EtO)_2PS_2$ at room temperature with 82% yield (Scheme 1). The complex 3 is analogous to the dithiophosphate complex $[Mo(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ [8], which is also crystallographically characterized. The solution phase IR spectrum shows two carbonyl bands at 1936 and 1840 cm^{-1} with equal intensity; this observation indicates that the two carbonyls are mutually *cis*. The room temperature ^{1}H-NMR spectrum shows a broad signal at δ 2.32 (methyl resonance of CH$_3$CN), an AM$_2$X$_2$ pattern of the allyl group and one equivalent resonance of the terminal carbon of the allyl group and one resonance of carbonyl group in the ^{13}C\{^{1}H\}-NMR spectrum, which suggests a similar intramolecular trigonal twist solution behavior to that of the crystallographically determined complex $[Mo(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ as shown, with one of the sulfur atom of the dithiophosphate ligand being *trans* to the allyl group.

The variable-temperature ^{1}H-NMR experiments of 3 were used to investigate the solution behavior. On cooling the CDCl$_3$ solutions of 3, the proton signals initially broaden and below 233 K the methyl resonance of CH$_3$CN and the *syn*- and *anti*-proton signals of the allyl moiety each begin to separate into two components. The intramolecular trigonal twist mechanism has been previously described for $[Mo(pd)(\eta^3-C_3H_5)(CO)_2(py)]$ [11b], $[Mo(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ [8] and other related complexes [10]. The line-shapes calculated from variable-temperature ^{1}H-NMR spectra of 3 yields a value of 11.5 ± 0.2 kcal mol^{-1} for $\Delta G^{\ddagger}$. Compared with other rearrangement complexes, the activation energy of 3 is similar to that of complex $[Mo(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ (11.6 kcal mol^{-1}) [8], is larger than that of complex $[W(\eta^3-C_3H_5)(CO)_2(dppe)I]$ (10.7 kcal mol^{-1}) [11a] and is smaller than that of complex $[Mo(pd)(\eta^3-C_3H_5)(CO)_2(py)]$ (14.3 kcal mol^{-1}) [11b].

2.3. Reaction of complex $[W(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ (3) with dppe

In order to compare the reactivity of $[W(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ (3) and Mo analogue and to synthesize the η^3-allyl *endo*, *exo*-stereoisomer [18] we have attempted the following reactions.

In the reaction of 3 with dppe, on adding CH$_2$Cl$_2$ solution of dppe to 3, the dppe bridged dinuclear complex $[W(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]_2(\mu\text{-dppe})$ (4) and η^1-dppe complex $[W(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}(\eta^1\text{-dppe})]$ (5) were obtained. The ratio of 4 to 5 was 4:1. An equimolar amount of a CH$_2$Cl$_2$ solution of dppe was added at room temperature to a

CH$_2$Cl$_2$ solution of 3 slowly, the mononuclear complex $[W(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]_2(\mu\text{-dppe})$ (4) was obtained as the sole product. The yellow compounds 4 and 5 are very air-stable and soluble in polar solvents. The FAB mass spectra of 4 show a parent peak corresponding to the [M$^+$] molecular mass. The solution phase IR spectrum (in CH$_2$Cl$_2$) shows the two carbonyls with equal intensity, which indicates that the two carbonyls are mutually *cis*. The ^{31}P\{^{1}H\} spectrum of 4 in CDCl$_3$ shows a resonance at δ 32.1 with a tungsten satellite (J(WP) 101.4 Hz), indicating phosphorus co-ordination of the dppe ligand and δ 108.5 (t, J(PP) 20.2 Hz) for the dithiophosphate ligand. The ^{13}C\{^{1}H\}-NMR spectrum of 4 reveals one doublet at the lowest field (δ 214.2 (d, ^2J(PC) 7.7 Hz), which is assigned to the terminal carbonyl groups. From an AM$_2$X$_2$ pattern of the allyl group in the ^{1}H-NMR spectra and one equivalent resonance of the terminal carbon of the allyl group and one resonance of carbonyl group in the ^{13}C\{^{1}H\}-NMR spectra, it seems that the dithiophosphato bidentate ligand and the two carbonyls lie in a horizontal plane, whereas the allyl group and the one phosphorus atom of the dppe ligand lie in *trans* positions above and below the plane. The two '$W(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}$' fragments were held together by a dppe ligand which is the only bridge between the two W atoms and suggests a structure different from that of the crystallographically determined complex $[Mo(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]_2(\mu\text{-NH}_2NH_2)$ [11].

If an equimolar amount of a CH$_2$Cl$_2$ solution of 3 was added at room temperature to a CH$_2$Cl$_2$ solution of dppe slowly, the mononuclear complex $[W(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}(\eta^1\text{-dppe})]$ (5) was obtained as the sole product. The FAB mass spectrum of 5 shows a base peak at *m/z* 864. The IR spectrum of 5 shows two carbonyl stretchings at 1934 and 1843 cm^{-1} with equal intensities, suggesting that the open face of the allyl is directed towards the two carbonyls as found in other structures of $(\eta^3-C_3H_5)$dicarbonylmolybdenum complexes [10c]. The ^{31}P\{^{1}H\} spectrum of 5 exhibits a resonance at δ 30.3 with a tungsten satellite (J(WP) 99.0 Hz), indicating phosphorus co-ordination of the dppe ligand. Upon refluxing CH$_3$CN for 72 h, no carbon monoxide was released to form the η^2-dppe *endo*, *exo*-stereoisomers complexes $[W(\eta^3-C_3H_5)(CO)\{\eta^2-S_2P(OEt)_2\}(\eta^2\text{-dppe})]$ in the case of complexes 5, 3 and dppe.

2.4. Conclusion

The structures of first dithiocarbamate Cr(0) (1) and dithiophosphate W(0) (2) have been determined by X-ray diffraction analyses. In the dithiophosphate complexes, the stability in W is larger than Mo but less soluble than those of Mo analogue. Complex $[W(CH_3CN)(\eta^3-C_3H_5)(CO)_2\{\eta^2-S_2P(OEt)_2\}]$ (3) reacted

with dppe in CH_2Cl_2 at room temperature to give a mixture of dinuclear dppe bridged complex $[W(\eta^3\text{-}C_3H_5)(CO)_2\{\eta^2\text{-}S_2P(OEt)_2\}]_2(\mu\text{-dppe})$ (**4**) and $[W(\eta^3\text{-}C_3H_5)(CO)_2\{\eta^2\text{-}S_2P(OEt)_2\}(\eta^1\text{-dppe})]$ (**5**). The variable-temperature ^1H-NMR experiments were used to confirm the intramolecular trigonal twist rotational behavior of **3** in the solution state.

3. Experimental

3.1. Materials

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. NMR spectra were recorded on an AM-500 WB FT-NMR spectrometer and are reported in units of δ (ppm) with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_6D_6, δ 7.15; C_2D_6CO, δ 2.04). IR spectra were measured on a Nicolate Avator-320 instrument and were referenced to a polystyrene standard, using cells equipped with calcium fluoride windows. Mass spectra were recorded on a JEOL SX-102A spectrometer. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. n-Hexane, diethyl ether, THF and benzene were distilled from sodium–benzophenone. Acetonitrile, dichloromethane were distilled from calcium hydride, and methanol from magnesium. All other solvents and reagents were of reagent grade and were used as received. Metal carbonyls, allyl bromide and $NH_4S_2P(OEt)_2$ were purchased from Strem, Merck and Janssen, respectively. The compounds $[Et_4N][Cr(\eta^2\text{-}S_2CNC_5H_{10})(CO)_4]$ [15] and $[Et_4N][W\{\eta^2\text{-}S_2P(OEt)_2(CO)_4]$ [8] were prepared according to the literature methods. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

3.2. (Acetonitrile)(η³-allyl)(dicarbonyl)(η²-diethyldithiophosphato)tungsten(II) (3)

Ten milliliter of CH_2Cl_2 was added to a 100 ml flask containing $[W(CH_3CN)_2(\eta^3\text{-}C_3H_5)(CO)_2(Br)]$ (0.442 g, 1.0 mmol) and $[NH_4][S_2P(OEt)_2]$ (0.203 g, 1.0 mmol) at ambient temperature. After stirring for 10 min, the solvent was removed in vacuo. The residue was abstracted by diethyl ether (2×5 ml). n-Hexane (40 ml) was added to the solution and a yellow–orange precipitate was formed. The precipitate was collected by filtration (G4) washed with cold n-hexane (2×10 ml) and then dried in vacuo yielding 0.42 g (82%) of **3**. Recrystallizations using a mixture of cold 20/1 n-hexane–diethyl ether give the yellow–orange crystalline product $[W(CH_3CN)(\eta^3\text{-}C_3H_5)(CO)_2\{\eta^2\text{-}S_2P(OEt)_2\}]$

(**3**). IR (CH_3CN) υ (CO) 1936(vs), 1840(vs); (KBr) υ (CO) 1916(vs), 1824(vs) cm^{-1}. $^{31}P\{^1H\}$-NMR (202 MHz, $CDCl_3$, 298 K): δ 108.9. ^1H-NMR (500 MHz, $CDCl_3$, 298 K): δ 1.41 (t, ^3J(HH) 7.1 Hz, 6H, OCH_2CH_3), 1.52 (d, J(HH) 8.9 Hz, 2H, Hanti of allyl), 2.32 (s, 3H, CH_3CN), 3.06 (br, 2H, Hsyn of allyl), 3.35 (m, 1H, CH of allyl), 4.44 (q, J(HH) 7.1 Hz, 4H, OCH_2). $^{13}C\{^1H\}$-NMR (125MHz, $CDCl_3$, 298K): δ 3.3 (s, CH_3CN), 15.8 (s, OCH_2CH_3), 56.7 (s, $CH=CH_2$), 63.9 (s, OCH_2), 75.5 (s, $CH_2=CH$), 119.5 (s, CH_3CN), 220.0 (s, CO). MS (FAB, NBA): m/z 507 $[M^+]$, 466 $[M^+-CH_3CN]$, 425 $[M^+-CH_3CN-C_3H_5]$, 397 $[M^+-CH_3CN-C_3H_5-CO]$, 369 $[M^+-CH_3CN-C_3H_5-2CO]$. Anal. Calc. for $C_{11}H_{18}NO_4PS_2W$: C, 26.04; H, 3.58; N, 2.76. Found: C, 26.34; H, 3.72; N, 2.98%.

3.3. Bis-[(η³-Allyl)(dicarbonyl)(η²-diethyldithiophosphato)tungsten(II)] [μ-bis-{(diphenyl–phosphine)ethane} (4)

3.3.1. Method A

Two milliliter CH_2Cl_2 solution of dppe (0.396 g, 1.0 mmol) was added to a flask containing a solution of **3** (0.523 g, 1.0 mmol) in MeCN (20 ml). After stirring for 10 min, a yellow–orange precipitate was formed. The precipitate was collected by filtration (G4) washed with n-hexane (2×10 ml) and then dried in vacuo yielding 0.70 g (51%) of **4** and 0.17 g (19%) of **5**. Recrystallizations using a mixture of 20/1 n-hexane–CH_2Cl_2 give a mixture of yellow–orange crystalline products $[W(\eta^3\text{-}C_3H_5)(CO)_2\{\eta^2\text{-}S_2P(OEt)_2\}]_2(\mu\text{-dppe})$ (**4**) and **5**.

3.3.2. Method B

Dppe (0.198 g, 0.5 mmol) was dissolved in CH_2Cl_2 (5 ml) and the solution was added slowly to a flask containing a solution of **3** (0.523 g, 1.0 mmol) in CH_2Cl_2 (10 ml) during a period of 5 min. The solution was stirred for 10 min and the solvent was removed in vacuo till about 5 ml. Methanol (15 ml) was added to the flask and the solution was stored at $-18\ ^\circ C$ for 12 h to give yellow precipitates. The precipitate was collected by filtration (G4) washed with n-hexane (2×10 ml) and then dried in vacuo yielding 0.69 g (96%) of **4** Spectroscopic data of **4**: IR (KBr) υ (CO) 1937(vs), 1857(vs) cm^{-1}. $^{31}P\{^1H\}$-NMR (202 MHz, $CDCl_3$, 298 K): δ 32.1 (dt, ^3J(PP) 20.2 Hz, J(WP) 101.4 Hz), 108.5 (t, J(PP) 20.2 Hz, PS_2). ^1H-NMR (500 MHz, $CDCl_3$, 298 K): δ 1.10 (t, ^3J(HH) 9.7 Hz, 12H, OCH_2CH_3), 1.76 (d, J(HH) 9.7 Hz, 4H, Hanti of allyl), 2.30, 2.81 (m, 4H, PCH_2), 3.48 (m, 2H, CH of allyl), 3.56 (m, 4H, Hsyn of allyl), 3.72 (m, 8H, OCH_2). $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$, 298 K): δ 15.8 (d, ^3J(PC) 8.6 Hz, OCH_2CH_3), 26.3 (dd, J(PC) 11.6, 11.1 Hz, PCH_2), 50.9 (br, $CH=CH_2$), 62.0 (d, ^2J(PC) 6.8 Hz, OCH_2), 74.2 (s, $CH_2=CH$), 214.6 (d, ^2J(PC) 7.7 Hz, CO). MS (FAB, NBA):

m/z 1331 [M$^+$], 1219 [M$^+$ −4CO]. Anal. Calc. for C$_{44}$H$_{54}$O$_8$P$_4$S$_4$W$_2$: C, 39.71; H, 4.09. Found: C, 39.84; H, 4.21%.

3.4. $(\eta^3$-Allyl$)(dicarbonyl)(\eta^2$-diethyldithiophosphato$)[\eta^1$-bis-$\{(diphenylphosphino)ethane\}]$ tungsten(II) (5)

Ten milliliter of CH$_2$Cl$_2$ solution of **3** (0.523 g, 1.0 mmol) was added slowly to a 100 ml flask containing dppe (0.396 g, 1.0 mmol) in CH$_2$Cl$_2$ (10 ml) during a period of 5 min at room temperature. A yellow–orange precipitate was formed. The precipitate was collected by filtration (G4) washed with n-hexane (2 × 10 ml) and then dried in vacuo yielding 0.87 g (95%) of (**5**). Recrystallization using a mixture of 20/1 n-hexane–CH$_2$Cl$_2$ to give the yellow–orange crystalline product [W(η^3-C$_3$H$_5$)(CO)$_2$\{η^2-S$_2$P(OEt)$_2$\}(η^1-dppe)] (**5**). IR (KBr) υ (CO) 1934(vs), 1843(vs) cm^{-1}. ^{31}P\{^{1}H\}-NMR (202 MHz, CDCl$_3$, 298 K): δ 30.3 (t, J(WP) 99.0 Hz, WPCH$_2$), 57.2 (br, PCH$_2$), 103.1 (br, PS$_2$). ^{1}H-NMR (500 MHz, CDCl$_3$, 298 K): δ 1.11, 1.23 (t, ^3J(HH) 7.1 Hz, 6H, OCH$_2$CH_3), 1.84 (d, J(HH) 9.5 Hz, 2H, Hanti of allyl), 2.28 (m, 4H, PCH$_2$), 3.23 (m, 4H, OCH_2), 3.50 (d, J(HH) 5.3 Hz, 2H, Hsyn of allyl), 4.23 (m, 1H, CH of allyl). ^{13}C\{^{1}H\}-NMR (125 MHz, CDCl$_3$, 298 K): δ 16.4 (d, ^3J(PC) 9.2 Hz, OCH$_2$CH_3), 27.3 (dd, J(PC) 11.6 Hz, PCH$_2$), 52.1 (br, CH=CH$_2$), 63.9, 64.8 (s, OCH$_2$), 73.3 (s, CH$_2$=CH), 214.6 (t, ^2J(PC) 8.7 Hz, CO). MS (FAB, NBA): m/z 864 [M$^+$], 836 [M$^+$ −CO], 808 [M$^+$ −2CO], 767 [M$^+$ −2CO−C$_3$H$_5$]. Anal. Calc. for C$_{35}$H$_{39}$O$_4$P$_3$S$_2$W: C, 48.62; H, 4.55. Found: C, 48.84; H, 4.78%.

Table 3
Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) for important atoms of **1**

Atom	x	y	z	B_{eg}
Cr	0.19514(6)	0.50000	0.32111(6)	3.63(3)
S1	0.36209(11)	0.42891(10)	0.57523(11)	4.09(5)
S2	0.16560(11)	0.60306(9)	0.51752(11)	3.77(5)
C1	0.0410(5)	0.4073(4)	0.2938(4)	4.22(21)
C2	0.0662(5)	0.5691(4)	0.1508(5)	4.48(23)
C3	0.2456(4)	0.4118(4)	0.2059(4)	4.79(24)
C4	0.3432(5)	0.5934(4)	0.3356(5)	4.47(23)
C5	0.3042(4)	0.5282(3)	0.6511(4)	3.35(17)
C6	0.3141(5)	0.6313(3)	0.8666(5)	4.61(22)
C7	0.4422(6)	0.7024(4)	0.9537(6)	6.1(3)
C8	0.5722(6)	0.6425(5)	1.0719(6)	7.1(3)
C9	0.6108(5)	0.5509(5)	0.9999(5)	6.0(3)
C10	0.4794(5)	0.4821(4)	0.9125(4)	5.01(24)
N1	0.3575(3)	0.5439(3)	0.8004(3)	4.04(17)
O1	−0.0567(4)	0.3519(3)	0.2647(4)	6.33(21)
O2	−0.0154(4)	0.6113(3)	0.0397(3)	6.93(21)
O3	0.2754(4)	0.3594(3)	0.1290(4)	7.59(23)
O4	0.4314(3)	0.649(3)	0.3391(5)	7.24(25)

Table 4
Selected bond distances (Å) and angles (°) for **2**

Bond lengths			
W–S	2.6093(14)	O–C(1)	1.435(5)
W–Sa	2.6093(14)	C(1)–C(2)	1.401(7)
W–C(3)	2.009(4)	C(3)–O(3)	1.141(5)
W–C(3)a	2.009(4)	C(4)–O(4)	1.183(6)
W–C(4)	1.910(5)	S–P	1.9859(17)
W–C(4)a	1.910(5)	P–Sa	1.9859(17)
P–O	1.579(3)	P–Oa	1.579(3)

| Bond angles			
S–W–Sa	75.95(5)	S–P–O	113.31(13)
S–W–C(3)	91.35(14)	S–P–Oa	113.27(12)
S–W–C(3)a	91.66(14)	Sa–P–O	113.27(12)
S–W–C(4)	98.27(16)	Sa–P–Oa	113.31(13)
S–W–C(4)a	174.21(16)	O–P–Oa	95.58(17)
Sa–W–C(3)	91.66(14)	P–O–C(1)	120.6(3)
Sa–W–C(3)a	91.35(14)	O–C(1)–C(2)	111.9(4)
Sa–W–C(4)	174.21(16)	W–C(3)–O(3)	176.8(4)
Sa–W–C(4)a	98.27(16)	W–C(4)–O(4)	178.7(4)
C(3)–W–C(3)a	176.17(20)	C(3)–W–C(4)	88.77(20)
C(3)–W–C(4)a	88.47(19)	C(3)a–W–C(4)	88.47(19)
C(3)a–W–C(4)a	88.77(20)	C(4)–W–C(4)a	87.51(22)
W–S–P	88.07(6)	S–P–Sa	107.90(10)

3.5. X-ray crystallography

3.5.1. Single-crystal X-ray diffraction analyses of **1** and **2**

Single crystals of **1** and **2** suitable from X-ray diffraction analyses were grown by recrystallization from 20:1 n-hexane–CH$_2$Cl$_2$. The diffraction data were collected at r.t. on an Enraf–Nonius CAD4 diffractometer equipped with graphite-monochromated Mo–K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package [19].

Table 5
Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3) for important atoms of **2**

Atom	x	y	z	B_{eg}
W	0	0.313843(18)	1/4	4.021(12)
S	0.08207(9)	0.18704(8)	0.15117(10)	5.43(6)
P	0	0.11499(11)	1/4	4.80(9)
O	−0.06702(22)	0.04959(17)	0.1769(3)	5.70(16)
C1	−0.1466(4)	0.0758(3)	0.0924(5)	7.5(3)
C2	−0.1548(4)	0.0236(3)	−0.0056(5)	8.9(4)
C3	−0.1145(3)	0.3180(3)	0.1238(4)	5.6(3)
O3	−0.1788(3)	0.3242(3)	0.0518(3)	9.61(24)
C4	0.0681(4)	0.3989(3)	0.1694(5)	6.3(3)
O4	0.1096(3)	0.45264(22)	0.1209(4)	10.0(3)

Table 6
Selected bond distances (Å) and angles (°) of Dithio-M(VIB)(0) complexes
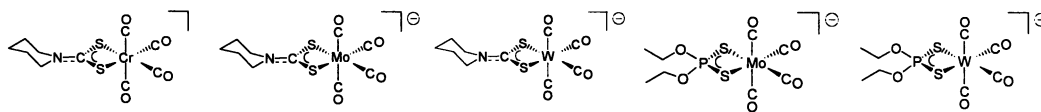
Bond distances					
M–S	2.4766(13)	2.5898(16)	2.6061(21)	2.622(16)	2.6102(14)
	2.4679(12)	2.5978(13)	2.5649(22)		
M–CO$_{trans}$	1.896(4)	2.017(5)	1.993(8)	2.023(4)	2.012(6)
	1.856(4)	2.033(5)	2.046(8)		
M–CO$_{cis}$	1.800(4)	1.951(5)	1.984(9)	1.922(5)	1.927(6)
	1.836(4)	1.930(5)	1.919(9)		
C–N	1.335(4)	1.336(5)	1.335(9)		
Bond angles					
S–X–S (X = C or P)	113.95(19)	115.77(24)	115.5(4)	108.98(9)	107.92(12)
S–M–S	70.84(5)	67.91(4)	67.83(6)	75.87(5)	76.07(7)
C$_{trans}$–M–C$_{trans}$	176.39(16)	175.20(18)	174.6(3)	176.04(17)	176.0(3)
C$_{cis}$–M–C$_{cis}$	89.64(17)	89.74(20)	89.5(4)	87.06(19)	87.5(4)
Ref.	This work	This work	[15]	[8]	This work

A suitable single crystal of **1** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with 2θ max 50.0°. Cell constants and other pertinent data were collected and are recorded in Table 1. Reflection data were collected using the $\theta/2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2.06 to 8.24° min^{-1}. The θ scan angle was determined for each reflection according to the equation $0.65 \pm 0.35 \tan \theta$. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 2110 unique measured data in which 1797 reflections with $I > 2\sigma(I)$ were considered observed. The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $\omega(|F_o| - |F_c|)^2$, where ω is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used [20]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1–2 Å^2 larger then the equivalent B_{iso} value of the atom to which they were bonded. The final residuals of this refinement were $R = 0.027$ and $R_w = 0.028$.

Selected bond distances and angles and selected final atomic coordinates are listed in Tables 2 and 3.

The procedure for **2** was similar to those for **1**. The final residuals of this refinement were $R = 0.026$ and $R_w = 0.019$ for **2**. Selected bond distances and angles and selected final atomic coordinates are listed in Tables 4 and 5. Tables of thermal parameters are given in the supplementary material.

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