ELSEVIER

Journal of Organometallic Chemistry 560 (1998) 1–6

Journal of Organometallic Chemistry

Dicarbonyl dithio ligand complexes of tungsten(II)

Simon Thomas [a], Edward R.T. Tiekink [b], Charles G. Young [a,*]

[a] *School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia*
[b] *Department of Chemistry, The University of Adelaide, Adelaide 5005, Australia*

Received 10 June 1997; received in revised form 16 January 1998

Abstract

Reaction of $LWI(CO)_n$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate, $n = 2$, 3] with $NH_4[S_2PR_2]$ [R = OEt, OPr^i, (–)-mentholate (R*), Ph] in acetonitrile or THF results in the formation of the dithio ligand complexes $LW(S_2PR_2\text{-}S)(CO)_2$. The yellow–orange, diamagnetic complexes exhibit IR spectra featuring two ν(CO) bands at ca. 1950 and 1840 cm^{-1} and ^{1}H-NMR spectra consistent with fluxional behavior in solution. Crystallographic characterisation of $LW\{S_2P(OPr^i)_2\text{-}S\}(CO)_2$ revealed a six-coordinate, distorted octahedral complex composed of a tungsten center coordinated by a monodentate dithiophosphate ligand, two *cis* carbonyl ligands, and a *facial*, tridentate L ligand. Unlike analogous complexes bearing strictly monodentate sulfur donor ligands, the $LW(S_2PR_2)(CO)_2$ complexes undergo reactions with oxygen atom donors to produce (carbonyl)oxo complexes of the type $LWO(S_2PR_2\text{-}S)(CO)$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten; Pyrazolylborate; Dicarbonyl; Dithio ligand; Crystal structure

---

1. Introduction

Only a relatively small number of monomeric dicarbonyl pyrazolylborate complexes of molybdenum and tungsten feature sulfur donor co-ligands. The first complexes of this type were reported by Trofimenko in 1971 [1]; they were prepared via reaction of $NEt_4[LM(CO)_3]$ with RSO_2Cl or RSCl, and included $LM(SR)(CO)_2$ (M = Mo, R = Ph, p-C_6H_4Me, p-C_6H_4Br; M = Mo and W, R = p-C_6H_4Cl). Many years later, Philipp et al. [2] reported the synthesis of closely related complexes, i.e. $LW(SR)(CO)_2$ (R = Me, Et, Pr^i, CH_2Ph, p-$C_6H_4NO_2$), by reaction of $LWI(CO)_2$ with thiols or thiolate salts. The structures of the p-nitrophenyl thiolate and benzyl thiolate derivatives revealed acute C–W–C angles [75.1(4) and 73.6(3)°, respectively], which can be ascribed to the optimization of π-back-bonding from tungsten to the carbonyl ligands [3–6]. These complexes also feature a W–S π-interaction, manifest by short W–S distances of ca. 2.3 Å and W–S–C angles of ca. 115°, which alleviates the electron deficiency of the metal center [2–6]. The complexes are non-fluxional on the NMR time scale and are chemically very inert. As well, Young et al. [7] have reported the preparation and structural characterization of $LW(S_2CNEt_2\text{-}S,S')(CO)_2$ from the reaction of $NEt_4[LW(CO)_3]$ and tetraethylthiuram disulfide. The seven-coordinate complex exhibits a severely distorted pentagonal bipyramidal structure and features a symmetrical, bidentate dithiocarbamate ligand. The complex is fluxional in solution and reacts with atom donor reagents such as pyridine *N*-oxide and cyclohexene sulfide to produce the oxo- and thio-W(IV) complexes $LWE(S_2CNEt_2\text{-}S,S')$ (E = O, S) [7,8]. While the analogous reaction between $NEt_4[LMo(CO)_3]$ and thiuram disulfides results in the formation of non-carbonyl complexes, $LMo(S_2CNR_2\text{-}S,S')(S_2CNR_2\text{-}S)$ [9,10], the reaction between $(L{-}N_3)MoI(CO)_3$ [$L{-}N_3$ = hydrotris(pyrazol-1-yl)borate, hydrotris(1,2,4-triazol-1-yl)borate, phenyltris(1,2,4-triazol-1-yl)borate] and $Ag[S_2CNEt_2]$ provides a route to complexes of the type $(L{-}N_3)Mo(S_2CNEt_2\text{-}S,S')(CO)_2$ [11].

---

* Corresponding author. Fax: +61 9347 5180.

PII S0022-328X(98)00463-X

We have been interested in developing precursors for atom transfer reactions leading to (carbonyl)oxo- and (carbonyl)thio-W(IV) complexes. To this end we have explored the synthesis and chemistry of a series of new dithio ligand complexes, $LW(S_2PR_2)(CO)_2$, which we report herein; the preparation and characterization of the complexes $LW(S_2PR_2)(CO)_2$ [R = OEt, OPr^i, (−)-mentholate (R*), Ph], along with the X-ray crystal structure of $LW\{S_2P(OPr^i)_2\}(CO)_2$, are described. In the solid state, $LW\{S_2P(OPr^i)_2\}(CO)_2$ adopts a six-coordinate structure which features a monodentate dithio ligand. In solution the complexes do indeed react with pyridine *N*-oxide to form $LWO(S_2PR_2)(CO)$ [12,13].

2. Results and discussion

The reactions at room temperature (r.t.) of $LWI(CO)_2$ and $NH_4[S_2PR_2]$ result in moderate yields of orange, diamagnetic $LW(S_2PR_2\text{-}S)(CO)_2$, according to Eq. (1). The complexes are also accessible from $LWI(CO)_3$ under reflux in acetonitrile.

$$LWI(CO)_2 + NH_4[S_2PR_2] \rightarrow LW(S_2PR_2)(CO)_2 + NH_4I \qquad (1)$$

The complexes are very soluble in chlorinated solvents and THF but insoluble in alcohols and hydrocarbon solvents. They are all air-stable in solution and the solid state over a period of days or weeks but the R = OEt, OPr^i, and R* derivatives are slowly oxidized to $LWO(S_2PR_2\text{-}S)(CO)$, which decarbonylate further over periods of weeks to form blue $LWO(S_2PR_2\text{-}S,S')$. All of the complexes react with pyridine *N*-oxide to form $LWO(S_2PR_2\text{-}S)(CO)$ [12,13]. This contrasts with the behavior of the analogous $LM(SR)(CO)_2$ (M = Mo, W) complexes, which are very stable, even under reflux, to a range of oxidizing agents [2].

Solid state and solution infrared spectra of the complexes (Table 1) reveal two strong bands at ca. 1950 and 1840 cm^{-1} which are assigned to the symmetric and asymmetric ν(CO) modes, respectively, of the *cis*-dicarbonyl unit. As well, the solid state IR spectra reveal features characteristic of L [ν(BH) ca. 2550, ν(C=N) ca. 1540 cm^{-1}] and the dithio ligand, e.g. a strong ν(P=S) band in the 634–658 cm^{-1} region, a medium intensity ν(P–S) band in the 521–557 cm^{-1} region, a strong $\nu(P\text{–}O_{alkyl})$ band in the 956–979 cm^{-1} region [14] and a medium intensity ν(P–Ph) band at 1450 cm^{-1} [15]. Similar ν(P=S) and ν(P–S) bands are observed at ca. 655 and 540 cm^{-1}, respectively, in complexes of the type $(\eta^5\text{-}C_5H_5)Fe(S_2PR_2\text{-}S)(CO)_2$, $(\eta^5\text{-}C_5H_4Me)Fe(S_2PR_2\text{-}S)(CO)_2$ and $(\eta^5\text{-}C_5Me_5)Fe(S_2PR_2\text{-}S)(CO)_2$ (R = OEt, OPr^i) [16].

Table 1
IR spectral data

Compound	ν(CO) (cm^{-1})			
	KBr		CH_2Cl_2	
$LW\{S_2P(OEt)_2\}(CO)_2$	1939	1825	1955	1840
$LW\{S_2P(OPr^i)_2\}(CO)_2$	1945	1835	1950	1840
$LW(S_2PR^*_2)(CO)_2$	1947	1840	1950	1838
$LW(S_2PPh_2)(CO)_2$	1947	1834	1950	1841

The ^1H-NMR spectra of the $LW(S_2PR_2)(CO)_2$ (R = OEt, OPr^i, Ph) complexes reveal a degree of fluxionality in solution. At r.t., the resonances due to R and two of the resonances due to L (3:6 ratio) are broadened considerably. At −60°C, the spectrum of $LW\{S_2P(OPr^i)_2\}(CO)_2$ exhibits sharp resonances indicative of molecular C_s symmetry; a single dithio ligand methine resonance indicates that the R groups straddle the mirror plane, as observed in the solid state structure (vide infra). Low temperature spectra also reveal a second species at ca. 10% concentration. The complex possesses C_s symmetry but the dithio ligand R groups lie in the mirror plane (there are two methine environments). Broadening and coalescence of the resonances from the major and minor species occurs at higher temperatures. In solution IR spectra, there are no ν(CO) bands which are directly attributable to this complex but there is evidence of bands partially concealed by those of the major species. The minor species may be a seven-coordinate isomer of $LW\{S_2P(OPr^i)_2\text{-}S\}(CO)_2$, viz. $LW\{S_2P(OPr^i)_2\text{-}S,S'\}(CO)_2$, or a monocarbonyl species such as $LW\{S_2P(OPr^i)_2\text{-}S,S'\}(CO)$ but we are unable to make a definitive assignment. Fluxional behavior was observed in the case of $LW(S_2CNEt_2)(CO)_2$, which adopts a seven-coordinate geometry in the solid state [7]. Fluxionality is not a feature of $LM(SR)(CO)_2$ (M = Mo, W) [2] complexes. A transient seven-coordinate species may be involved in the fluxional process at r.t. The ^1H-NMR spectrum of $LW(S_2PR^*_2)(CO)_2$ is indicative of the presence of a single isomer with molecular C_1 symmetry.

The orange dithiophosphate complexes exhibit absorption spectra with λ_{max} at 860–870 nm (ε 80–90 M^{-1} cm^{-1}), 390–410 nm (ε ca. 8×10^3 M^{-1} cm^{-1}) and 320 nm (ε ca. 10^4 M^{-1} cm^{-1}). For $LW(S_2PPh_2)(CO)_2$, absorption maxima are observed at 860 nm (ε 80 M^{-1} cm^{-1}), 420 nm (ε 3.2×10^3 M^{-1} cm^{-1}) and 350 nm (ε 1.7×10^4 M^{-1} cm^{-1}). The low energy bands may be assigned to d–d transitions on the basis of their extinction coefficients.

The structure of $LW\{S_2P(OPr^i)_2\}(CO)_2$ has been determined by X-ray crystallography. A view of the molecule and the atom numbering scheme are shown in Fig. 1 and selected bond distances and angles are presented in Table 2. The monomeric, six-coordinate complex exhibits a distorted octahedral geometry and is composed of two *cis* terminal carbonyl ligands, a monodentate di-iso-propyldithiophosphate ligand, and

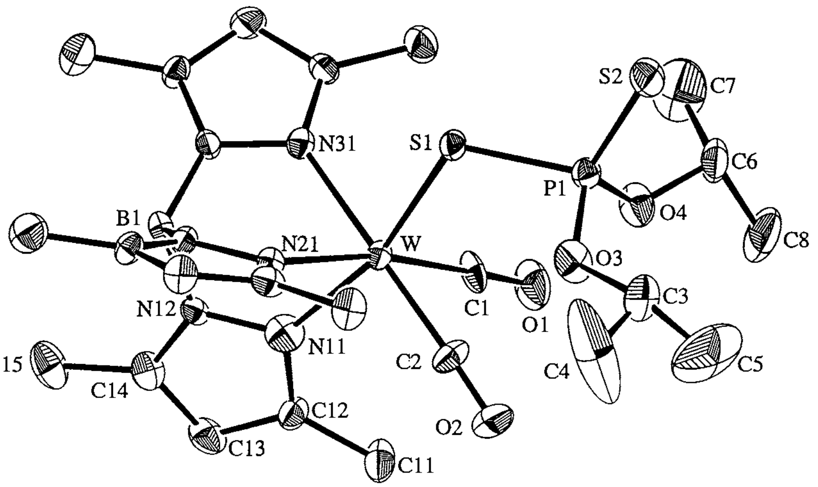

Fig. 1. Molecular structure of $\text{LW}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}(\text{CO})_2$. The numbering of the pyrazole rings containing N21 and N31 follows that shown for the ring containing N11. Hydrogen atoms have been excluded for clarity.

a *facial*, tridentate L ligand. The greatest angular distortions from an ideal octahedral geometry are the acute C1–W–C2 angle of 75.6(5)° and the N11–W–S1 angle of only 165.1(4)°. Acute C–W–C angles are a common feature of LWX(CO)_2 (X = monoanionic ligand) complexes, and arise as a consequence of optimal π-back-bonding from the metal to the carbonyl ligands [2–6]. The W–S1 bond distance of 2.361(5) Å is shorter than the distance typical of W–S single bonds [17] but significantly longer than the W–S distances in $\text{LW(S-}p\text{-C}_6\text{H}_4\text{NO}_2)(\text{CO})_2$ [2.320(2) Å] and $\text{LW(SCH}_2\text{Ph)(CO)}_2$ [2.298(2) Å] [2]. The W–S1–P1 angle of 115.5(2)° is slightly greater than the tetrahedral angle of 109.4° expected for an sp^3 hybridized sulfur atom and similar to the W–S–C angles of $\text{LW(S-}p\text{-C}_6\text{H}_4\text{NO}_2)(\text{CO})_2$ [116.8(3)°] and $\text{LW(SCH}_2\text{Ph)(CO)}_2$ [114.7(3)°], compounds proposed to have W–S bonds with π-character [2,18]. The metric parameters associated with the dithiophosphate-tungsten unit are consistent with a degree of π-bonding between tungsten and sulfur, but less than the case for related LW(SR)(CO)_2 complexes [2]. A pseudo-mirror plane bisects the carbonyl ligands and contains the W–S–P=S unit and the dimethylpyrazole ring containing N11 [the mean deviation of the atoms from the plane is 0.11 Å and the max. displacement = 0.32(1) Å for C(15)]. The dithiophosphate oxygen atoms O3 and O4 are directed toward the carbonyl ligands and as a consequence S2 is directed away from the metal center, i.e. the ligand adopts an *exo* conformation. A very similar arrangement is observed in the dicarbonyl complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}(\text{CO})_2$ [19]. The di-iso-propyldithiophosphate ligand is not completely symmetrically aligned with the mirror plane as evidenced by discrepancies in the torsion angles W–S1–P1–O3 [−61.6(4)°] and W–S1–P1–O4 [47.2(5)°]. Monodentate dialkyldithiophosphate coordination is rare [20], with examples including $\text{Ni}\{\text{S}_2\text{P(OEt)}_2\}_2\text{-(Me}_2\text{phen)}$ (Me_2phen = 1,9-dimethylphenanthroline) [21], $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{\text{S}_2\text{P-(OPr}^i)_2\}(\text{CO})_2$ [19] and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(S}_2)\{\text{S}_2\text{P(OEt)}_2\}$ [22]. Monodentate coordination of the ligand in $\text{LW}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}(\text{CO})_2$ and bidentate coordination in $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}(\text{CO})_2$ [23] may reflect steric encumbrances in the pyrazolylborate species. The P1–S2 bond distance of 1.935(4) Å is indicative of a P=S double bond and compares well with previously reported examples possessing this moiety, e.g. $[\text{Pr}^i_2\text{P(S)S}]_2$, P=S 1.9312(8) Å [24], $[(\text{Pr}^i\text{O})_2\text{P(S)S}]_2$, P=S 1.908(3) Å [25], $\text{Ni}\{\text{S}_2\text{P(OEt)}_2\}_2(\text{Me}_2\text{phen})$, P=S 1.94(1) Å [21], $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}\{\text{S}_2\text{P}(\text{OPr}^i)_2\}(\text{CO})_2$, P=S 1.944(2) Å [19] and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(S}_2)\{\text{S}_2\text{P(OEt)}_2\}$, P=S 1.935(7) Å [22].

The reactivity of the $\text{LW(S}_2\text{PR}_2)(\text{CO})_2$ complexes toward oxygen atom donors stands in stark contrast to the inertness of the related LW(SR)(CO)_2 complexes. At least two factors may account for the difference in reactivity. Firstly, the apparently greater degree of π-bonding between tungsten and sulfur in the LW(SR)(CO)_2 complexes versus the $\text{LW(S}_2\text{PR}_2)(\text{CO})_2$ complexes may stabilize the former with respect to the latter. Secondly, it is possible that the dithio ligands of $\text{LW(S}_2\text{PR}_2)(\text{CO})_2$ function in an ambidentate fashion, producing seven-coordinate $\text{LW(S}_2\text{PR}_2\text{-}S,S')(\text{CO})_2$ or the monocarbonyl $\text{LW(S}_2\text{PR}_2\text{-}S,S')(\text{CO})$, which is activated towards reaction. We have already noted that $\text{LW(S}_2\text{CNEt}_2)(\text{CO})_2$, which features a bidentate dithiocarbamate ligand in the solid state (but is fluxional in solution), reacts with oxygen and sulfur atom donors, possibly for a related reason. This mode of activation would not be possible for the strictly monodentate sulfur donor ligand complexes.

Table 2
Selected bond distances (Å) and angles (°) for $LW\{S_2P(OPr^i)_2\}(CO)_2$

Bond distance (Å)					
W–S1	2.361(5)	W–C1	1.983(9)	W–C2	1.945(8)
W–N11	2.09(2)	W–N21	2.204(7)	W–N31	2.229(8)
C1–O1	1.14(1)	C2–O2	1.16(1)	P1–S1	2.064(6)
P1–S2	1.935(4)				
Bond angle (°)					
S1–W–C1	98.5(7)	S1–W–C2	95.8(8)		
S1–W–N11	165.1(4)	S1–W–N21	89.9(3)		
S1–W–N31	87.5(4)	S1–W–C1	98.5(7)		
S1–W–C2	95.8(8)	C1–W–C2	75.6(5)		
C1–W–N11	93.5(8)	C1–W–N21	169.9(6)		
C1–W–N31	100.0(4)	C2–W–N11	95.6(9)		
C2–W–N21	98.1(4)	C2–W–N31	174.8(6)		
N11–W–N21	79.1(5)	N11–W–N31	81.8(6)		
N21–W–N31	85.8(3)	W–C1–O1	174.0(1)		
W–C2–O2	170.0(1)	W–S1–P1	115.5(2)		
S1–P1–S2	114.1(3)				

3. Experimental

Unless otherwise stated, all manipulations were performed under an atmosphere of purified N_2 using standard Schlenk techniques. Solvents were dried, distilled and deoxygenated before use. A literature method was employed in the synthesis of $LWI(CO)_2$ [2]. All other chemicals were obtained from Aldrich and were laboratory grade or above. IR spectra were recorded using Perkin-Elmer 983G or Shimadzu IR-408 spectrophotometers calibrated with polystyrene. ^{1}H-NMR spectra were obtained using a Varian 300 MHz FT-NMR spectrometer. Electronic spectra were recorded using a Perkin-Elmer 1430 spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

3.1. *Synthesis of dicarbonyl(diethyldithiophosphatoS){hydrotris(3,5-dimethylpyrazol-1-yl)borato}-tungsten(II)*

A suspension of $LWI(CO)_2$ (1.91 g, 2.88 mmol) and $NH_4[S_2P(OEt)_2]$ (0.61 g, 2.88 mmol) in acetonitrile (15 ml) was stirred at r.t. for 20 min. The mixture was reduced to dryness and the residue dissolved in dichloromethane, then filtered through a short bed of silica. The filtrate was reduced to dryness, then purified by column chromatography on silica gel using 1:1 dichloromethane:hexane as eluent. The orange fraction was collected, reduced to dryness and recrystallized from dichloromethane/hexane. The orange crystals were filtered, washed with cold hexane (5 ml) and dried in vacuo. Yield 0.45 g, 22%.

Anal. Calc. for $C_{21}H_{32}BN_6BO_4PS_2W$: C 34.92, H 4.47, N 11.64, S 8.88. Found: C 35.01, H 4.42, N 11.65, S 8.80%. IR (KBr, cm^{-1}): ν(BH) 2550, ν(CO) 1939, 1825, ν(CN) 1543, 951, 644. ^{1}H-NMR ($CDCl_3$): δ 1.20–1.55 (br s, 6H, 2 CH_3 of $S_2P(OEt)_{2-}$), 2.15 (br s, 6H, 2 CH_3 of L), 2.41 (s, 3H, CH_3 of L), 2.63 (br s, 3H, CH_3 of L), 2.83 (s, 6H, 2 CH_3 of L), 4.05–4.45 (br s, 4H, 2 CH_2 of $S_2P(OEt)_{2-}$), 5.90 (s, 2H, 2 CH of L), 6.07 (s, 1H, CH of L). Electronic spectrum (CH_2Cl_2): 860 (80), 390 (9.0×10^3), 320 nm (ε 9.8×10^3 M^{-1} cm^{-1}).

3.2. *Synthesis of dicarbonyl(di-iso-propyldithiophosphato-S){hydrotris(3,5-dimethylpyrazol-1-yl)borato}-tungsten(II)*

A suspension of $LWI(CO)_2$ (1.50 g, 2.26 mmol) and $NH_4[S_2P(OPr^i)_2]$ (0.53 g, 2.26 mmol) in acetonitrile (30 ml) was stirred at r.t. for 30 min. The reaction was worked up as described above for $LW\{S_2P(OEt)_2\}(CO)_2$ to yield yellow crystals. Yield 0.69 g, 41%.

Anal. Calc. for $C_{23}H_{36}BN_6O_4PS_2W$: C 36.82, H 4.84, N 11.20, S 8.55. Found: C 36.86, H 4.90, N 11.30, S 8.62%. IR (KBr, cm^{-1}): ν(BH) 2550, ν(CO) 1945, 1835, ν(CN) 1543, ν(P–O$_{alkyl}$) 956, 979, ν(P=S) 634, ν(P–S) 544. ^{1}H-NMR ($CDCl_3$, 25°C): δ 1.05–1.65 (br s, 12H, 4 CH_3 of $S_2P(OPr^i)_{2-}$), 2.15 (br s, 6H, 2 CH_3 of L), 2.41 (s, 3H, CH_3 of L), 2.61 (br s, 3H, CH_3 of L), 2.81 (s, 6H, 2 CH_3 of L), 4.80–5.10 (br s, 2H, 2CH of $S_2P(OPr^i)_{2-}$), 5.89 (s, 2H, 2 CH of L), 6.06 (s, 1H, CH of L). ^{1}H-NMR ($CDCl_3$, −60°C): major, δ 1.36 (d, 6H, $J=7.3$ Hz, 2 CH_3 of $S_2P(OPr^i)_{2-}$), 1.38 (d, 6H, $J=7.3$ Hz, 2 CH_3 of $S_2P(OPr^i)_{2-}$), 2.07 (s, 6H, 2 CH_3 of L), 2.37 (s, 3H, CH_3 of L), 2.57 (s, 3H, CH_3 of L), 2.80 (s, 6H, 2 CH_3 of L), ca. 5.00 (m, 2H, 2CH of $S_2P(OPr^i)_{2-}$), 5.91 (s, 2H, 2 CH of L), 6.12 (s, 1H, CH of L); minor, δ 0.95 (d, 6H, $J=6.5$ Hz, 2CH_3 of $S_2P(OPr^i)_{2-}$), 1.05 (d, 6H, $J=6.5$ Hz, 2CH_3 of $S_2P(OPr^i)_{2-}$), 1.92 (s, 6H, 2 CH_3 of L), 2.33 (s, 3H, CH_3 of L), 2.45 (s, 3H, CH_3 of L), 2.73 (s, 6H, 2 CH_3

of L), 4.60 (m, 1H, C*H* of $S_2P(OPr^i)_{2-}$), 4.90 (m, 1H, C*H* of $S_2P(OPr^i)_{2-}$), 5.88 (s, 2H, 2 C*H* of L), 7.24 (s, 1H, C*H* of L). Electronic spectrum (CH_2Cl_2): 870 (90), 390 (8.0×10^3), 320 nm (ε 1.0×10^4 M^{-1} cm^{-1}).

3.3. Synthesis of ammonium di-(−)-menthyldithiophosphate, $NH_4[S_2PR^*_2]$ [$R^* = (-)$mentholate]

A suspension of phosphorus pentasulfide (2.40 g, 5.40 mmol) and (−)-menthol (6.71 g, 42.9 mmol) in toluene (80 ml) was refluxed for 1.5 h. The reaction mixture was allowed to cool and any solid residue was removed by filtration. Ammonia gas was bubbled through the filtrate for 10 min and hexane (80 ml) added to precipitate the product. The white crystalline solid was filtered off, washed with hexane (20 ml) and dried in vacuo. Yield 5.20 g, 57%.

Anal. Calc. for $C_{20}H_{42}NO_2PS_2$: C 56.70, H 9.99, N 3.31, S 15.14. Found: C 56.80, H 9.95, N 3.26, S 15.06%. IR (KBr) ν: 3420br, 3105br, 2955s, 2926s, 2870m, 1453m, 1414s, 1387s, 1012m, 996m, 965s, 930m, 882m, 870m, 818m, 672s, 570m cm^{-1}.

3.4. Synthesis of dicarbonyl(dimenthyldithiophosphato-S){hydrotris(3,5-dimethylpyrazol-1-yl)borato}-tungsten(II)

A suspension of $LWI(CO)_2$ (1.00 g, 1.51 mmol) and $NH_4[S_2PR^*_2]$ (1.82 g, 2.75 mmol) in acetonitrile (40 ml) was stirred at r.t. for 30 min. The reaction was worked up as described for $LW\{S_2P(OEt)_2\}(CO)_2$ to yield yellow crystals. Yield 1.87 g, 72%.

Anal. Calc. for $C_{37}H_{60}BN_6O_4PS_2W$: C 47.14, H 6.42, N 8.92, S 6.80. Found: C 47.22, H 6.38, N 9.02, S 6.93%. IR (KBr, cm^{-1}): ν(BH) 2557, ν(CO) 1947, 1840, ν(CN) 1544, ν($P{-}O_{alkyl}$) 951, 983, ν(P=S) 658, ν(P–S) 557. ^{1}H-NMR ($CDCl_3$): δ 0.8–2.7 (m, 18H of mentholate), 2.13 (s, 6H, 2 CH_3 of L), 2.41 (s, 3H, CH_3 of L), 2.59 (s, 13H, CH_3 of L), 2.80 (s, 13H, CH_3 of L), 2.81 (s, 13H, CH_3 of L), 4.25–4.45 (m, 2H, 13OC*H* of mentholate), 5.89 (s, 2H, 2 C*H* of L), 6.05 (s, 1H, C*H* of L). Electronic spectrum (CH_2Cl_2): 860 (90), 410 (7.2×10^3), 320 nm (ε 1.1×10^4 M^{-1} cm^{-1}).

3.5. Synthesis of dicarbonyl(diphenyldithiophosphinato-S) {hydrotris(3,5-dimethylpyrazol-1-yl)borato}-tungsten(II)

A suspension of $LWI(CO)_2$ (1.92 g, 2.89 mmol) and $NH_4[S_2PPh_2]$ (0.77 g, 2.89 mmol) in tetrahydrofuran (60 ml) was stirred at r.t. for 30 min, whereupon an orange precipitate formed. The mixture was reduced to dryness and the residue was column chromatographed on silica gel using 3:1 dichloromethane:hexane as eluent. The orange fraction was collected, reduced to dryness, then recrystallized from dichloromethane/hexane to give orange crystals. These were filtered, washed with hexane (5 ml) and dried in vacuo. Yield 1.40 g, 62%.

Anal. Calc. for $C_{29}H_{32}BN_6O_2PS_2W$: C 44.30, H 4.10, N 10.69, S 8.15. Found: C 44.36, H 4.18, N 10.64, S 8.09%. IR (KBr, cm^{-1}): ν(BH) 2555, ν(CO) 1947, 1834, ν(CN) 1543, ν(P–Ph) 1450, ν(P=S) 648, ν(P–S) 521. ^{1}H-NMR ($CDCl_3$): δ 1.87 (br s, 6H, 2 CH_3 of L), 2.36 (s, 3H, CH_3 of L), 2.56 (s br, 3H, CH_3 of L), 2.80 (s, 6H, 2 CH_3 of L), 5.83 (br s, 2H, 2 C*H* of L), 6.03 (s, 1H, C*H* of L), 7.40 (br m, 6H, Ph), 8.04 (br m, 4H, Ph). Electronic spectrum (CH_2Cl_2): 860 (80), 420 (3.2×10^3), 350 nm (ε 1.7×10^4 M^{-1} cm^{-1}).

3.6. Crystal structure determination of $LW\{S_2P(OPr^i)_2\}(CO)_2$

Orange crystals of $LW\{S_2P(OPr^i)_2\}(CO)_2$ were grown by slow diffusion of hexane into a saturated

Table 3
Fractional atomic coordinates for $LW\{S_2P(OPr^i)_2\}(CO)_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
W	0.10793(2)	−0.23173(3)	0
S1	0.1018(2)	−0.2052(5)	0.1747(4)
S2	0.1429(2)	−0.3072(3)	0.4015(2)
P1	0.1436(2)	−0.3387(3)	0.2593(2)
O1	0.2478(4)	−0.2958(9)	−0.0120(12)
O2	0.1217(4)	−0.5115(7)	−0.0043(15)
O3	0.1050(4)	−0.4508(7)	0.2263(6)
O4	0.2095(4)	−0.3632(9)	0.2149(6)
N11	0.0962(7)	−0.2192(15)	−0.1550(12)
N12	0.0597(4)	−0.1330(7)	−0.2000(5)
N21	0.0069(3)	−0.2151(7)	−0.0106(9)
N22	−0.0190(4)	−0.1236(7)	−0.0650(6)
N31	0.1094(4)	−0.0298(7)	−0.0132(11)
N32	0.0663(4)	0.0295(7)	−0.0708(5)
C1	0.1973(4)	−0.2667(11)	−0.0104(18)
C2	0.1131(5)	−0.4082(7)	0.0036(19)
C3	0.1022(9)	−0.5646(12)	0.2828(9)
C4	0.0464(11)	−0.6205(23)	0.2561(20)
C5	0.1554(13)	−0.6415(17)	0.2541(18)
C6	0.2677(6)	−0.3469(12)	0.2674(10)
C7	0.2881(8)	−0.2175(17)	0.2531(16)
C8	0.3107(7)	−0.4338(15)	0.2169(14)
C11	0.1702(7)	−0.3832(14)	−0.2253(8)
C12	0.1244(6)	−0.2838(11)	−0.2374(9)
C13	0.1004(5)	−0.2355(12)	−0.3260(7)
C14	0.0606(5)	−0.1424(11)	−0.2999(8)
C15	0.0236(6)	−0.0648(12)	−0.3658(8)
C21	−0.0318(5)	−0.3857(10)	0.0952(9)
C22	−0.0408(5)	−0.2771(9)	0.0299(6)
C23	−0.0956(4)	−0.2264(9)	−0.0009(23)
C24	−0.0810(5)	−0.1299(10)	−0.0600(8)
C25	−0.1242(6)	−0.0467(11)	−0.1134(11)
C31	0.2042(6)	0.0297(10)	0.0864(10)
C32	0.1481(5)	0.0575(9)	0.0222(8)
C33	0.1281(5)	0.1690(9)	−0.0094(14)
C34	0.0776(5)	0.1494(9)	−0.0691(8)
C35	0.0386(5)	0.2377(11)	−0.1244(10)
B1	0.0223(5)	−0.0462(11)	−0.1328(8)

dichloromethane solution of the complex. Intensity data for an orange crystal (0.08 × 0.24 × 0.24 mm) were collected at r.t. on a Rigaku AFC6R employing Mo–K_α radiation ($\lambda = 0.71073$ Å) and the ω:2θ scan technique. The 4163 unique data (θ_{max} 27.5°) were corrected for Lorentz and polarisation effects [26] as well as for absorption employing an empirical procedure [27]; the range of transmission factors was 0.948–1.000. A total of 2630 data satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for $LW\{S_2P(OPr^i)_2\}(CO)_2$: $C_{23}H_{36}BN_6O_4PS_2W$, $M = 750.3$, orthorhombic, space group $Pna2_1$, $a = 21.699(2)$, $b = 11.002(7)$, $c = 13.3831(9)$ Å, $V = 3195(2)$ Å^3, $Z = 4$, $D_{calc.} = 1.560$ g cm^{-3}, $F(000) = 1496$, $\mu = 38.37$ cm^{-1}, $R = 0.031$, $R_w = 0.029$.

The structure was solved by direct methods [28] and refined by a full-matrix least-squares procedure based on F [26]. All non-H atoms were refined with anisotropic displacement parameters and H atoms were included in the model at their calculated positions (C–H 0.97, B–H 0.95 Å). The refinement was continued until convergence employing sigma weights, i.e. $1/\sigma^2(F)$, when $R = 0.031$ and $R_w = 0.029$. The maximum peak in the final difference map was 0.71 e Å^{-3} and the analysis of variance showed no special features. Refinement of the other hand resulted in significantly larger values for the residuals. Fractional atomic coordinates are listed in Table 3, while selected interatomic parameters are collected in Table 2. The crystallographic numbering scheme for the molecule is shown in Fig. 1 which was drawn with ORTEP [29] at 30% probability ellipsoids.

4. Supplemental material available

A copy of the CIF and the observed and calculated structure factors are available from E.R.T. Tiekink at the following e-mail address (etiekink@chemistry.adelaide.edu.au).

Acknowledgements

We gratefully acknowledge the financial support of the Australian Research Council.

References

[1] S. Trofimenko, Inorg. Chem. 10 (1971) 504.

[2] C.C. Philipp, C.G. Young, P.S. White, J.L. Templeton, Inorg. Chem. 32 (1993) 5437.

[3] J.L. Templeton, B.C. Ward, J. Am. Chem. Soc. 102 (1980) 6568.

[4] P. Kubácek, R. Hoffmann, J. Am. Chem. Soc. 103 (1981) 4320.

[5] J.L. Templeton, P.B. Winston, B.C. Ward, J. Am. Chem. Soc. 103 (1981) 7713.

[6] J.L. Templeton, J.L. Caldarelli, S. Feng, C.C. Philipp, M.B. Wells, B.E. Woodworth, P.S. White, J. Organomet. Chem. 478 (1994) 103.

[7] C.G. Young, M.A. Bruck, P.A. Wexler, M.D. Carducci, J.H. Enemark, Inorg. Chem. 31 (1992) 587.

[8] C.G. Young, M.A. Bruck, J.H. Enemark, Inorg. Chem. 31 (1992) 593.

[9] C.G. Young, S.A. Roberts, J.H. Enemark, Inorg. Chim. Acta 114 (1986) L7.

[10] C.G. Young, S.A. Roberts, J.H. Enemark, Inorg. Chem. 25 (1986) 3667.

[11] K.-B. Shiu, J.Y. Lee, Y. Wang, M.-C. Cheng, Inorg. Chem. 32 (1993) 3565.

[12] S. Thomas, E.R.T. Tiekink, C.G. Young, Organometallics 15 (1996) 2428.

[13] A.A. Eagle, S. Thomas, C.G. Young, in: E.I. Stiefel, K. Matsumoto (Eds.), Transition Metal Sulfur Chemistry: Biological and Industrial Significance, ACS Symp. Ser. no. 653, Am. Chem. Soc., Washington, DC, 1996, p. 324.

[14] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, 4th ed., Wiley, New York, 1981, p. 176.

[15] D.H. Williams, I. Fleming, Spectroscopic Methods in Organic Chemistry, 4th ed., McGraw Hill, London, 1989, p. 56.

[16] M. Morán, I. Cuadrado, J. Organomet. Chem. 295 (1985) 353.

[17] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. (1989) S1.

[18] M.T. Ashby, Comments Inorg. Chem. 10 (1990) 297.

[19] J. Sanz-Aparicio, S. Martínez-Carrera, S. García-Blanco, Acta Crystallogr. Sect. C 42 (1986) 1121.

[20] I. Haiduc, Rev. Inorg. Chem. 3 (1981) 353.

[21] P.S. Shetty, Q. Fernando, J. Am. Chem. Soc. 92 (1970) 3964.

[22] R. Mercier, J. Douglade, B. Viard, Acta Crystallogr. Sect. B 37 (1981) 949.

[23] S. Woodward, U. Riaz, M.D. Curtis, B.S. Haggerty, A.L. Rheingold, Organometallics 9 (1990) 2703.

[24] A.C. Gallacher, A.A. Pinkerton, Acta Crystallogr. Sect C 48 (1992) 2085.

[25] S.L. Lawton, Inorg. Chem. 9 (1970) 2269.

[26] TEXSAN, Structure Analysis Package, Molecular Structure Corporation, TX, 1992.

[27] N. Walker, D. Stuart, Acta Crystallogr. Sect. A 39 (1983) 158.

[28] G.M. Sheldrick, SHELXS86, Program for the automatic solution of crystal structure, University of Göttingen, Germany, 1986.

[29] C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.