

( $\mu$ -Thio)ditungsten(II) Complexes: Syntheses and Crystal Structures of  $[\{\text{HB}(\text{Me}_2\text{C}_3\text{N}_2\text{H})_3\}\text{W}(\text{CO})_2]_2(\mu\text{-S})$  and  $[\{\text{HB}(\text{Pr}^i\text{C}_3\text{N}_2\text{H}_2)_3\}\text{W}(\text{CO})_2]_2(\mu\text{-S})$

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Blue, diamagnetic  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_2]_2(\mu\text{-S})$  (**1**) and  $[\{\text{HB}(\text{Pr}^i\text{pz})_3\}\text{W}(\text{CO})_2]_2(\mu\text{-S})$  (**2**) are formed upon reaction of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WBr}(\text{CO})_2$ ,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WH}(\text{CO})_3$ , or  $\{\text{HB}(\text{Pr}^i\text{pz})_3\}\text{WH}(\text{CO})_3$  with propylene sulfide in refluxing 1,2-dichloroethane. Both complexes have been characterized by analytical, mass spectrometric, IR and <sup>1</sup>H NMR spectroscopic, and X-ray crystallographic studies. Crystal data for **1**: monoclinic space group  $C2/c$ ,  $a = 20.315(5)$  Å,  $b = 14.450(3)$  Å,  $c = 13.796(2)$  Å,  $\beta = 103.02(2)^\circ$ , and  $V = 3945(1)$  Å<sup>3</sup> with  $Z = 4$ . Crystal data for **2**: monoclinic space group  $P2_1$ ,  $a = 11.433(5)$  Å,  $b = 14.354(7)$  Å,  $c = 15.058(4)$  Å,  $\beta = 103.98(3)^\circ$ , and  $V = 2397(1)$  Å<sup>3</sup> with  $Z = 2$ . The structures were each refined by a full-matrix least-squares procedure to  $R = 0.027$  for 3290 reflections with  $I \geq 3.0\sigma(I)$  for **1** and  $R = 0.024$  (4245 reflections) for **2**. The dinuclear complexes are composed of distorted octahedral tungsten centers coordinated by *fac*-tris(pyrazolyl)borate, carbonyl, and bridging thio ligands. The triatomic  $[\text{W}_2\text{S}]^{2+}$  cores are characterized by short W-S distances (2.1809(3) Å for **1**, 2.173(3) and 2.184(3) Å for **2**) and nearly linear W-S-W bond angles ( $171.6(1)^\circ$  for **1** and  $175.3(1)^\circ$  for **2**).

The isolation and partial characterization of a number of pterin-containing tungsten enzymes from hyperthermophilic Archaea has stimulated a renewed interest in tungsten-sulfur chemistry.<sup>1</sup> The requirement of thiols in the isolation of active aldehyde: ferredoxin oxidoreductase<sup>2</sup> and EXAFS evidence supporting the presence of a  $[\text{WO}_2]^{2+}$  center in an inactive form of this enzyme<sup>3</sup> are consistent with thio coordination in the active enzyme. Recently, we described the synthesis and characterization of the novel oxothio- and dithiotungsten(VI) complexes,  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WOSCl}$  and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WS}_2\text{Cl}$  [ $\text{HB}(\text{Me}_2\text{pz})_3^-$  = hydrotris-(3,5-dimethyl-1-pyrazolyl)borate anion].<sup>4</sup> These complexes provide spectroscopic benchmarks for the interpretation of enzyme spectra and an entry into tungstoenzyme model chemistry.<sup>1</sup> They are formed in modest yield by reaction of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WO}_2\text{Cl}$  with boron sulfide in 1,2-dichloroethane.<sup>4</sup> This paper describes the synthesis and characterization of the binuclear ( $\mu$ -thio)ditungsten(II) complexes  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_2]_2(\mu\text{-S})$  (**1**) and  $[\{\text{HB}(\text{Pr}^i\text{pz})_3\}\text{W}(\text{CO})_2]_2(\mu\text{-S})$  (**2**) [ $\text{HB}(\text{Pr}^i\text{pz})_3^-$  = hydrotris(3-isopropyl-1-pyrazolyl)borate anion], produced in attempts to develop alternative syntheses for oxothio- and dithiotungsten(VI) complexes, in this case from low-valent carbonyltungsten starting materials (vide infra). It also reports the first X-ray crystal structures of compounds containing the rare, multiply-bonded, near-linear  $[\text{WSW}]^{2+}$  core.

Compounds containing linear or near-linear, multiply-bonded  $[\text{MSM}]^{++}$  cores are known for vanadium,<sup>5</sup> chromium,<sup>6,7</sup> molybdenum,<sup>8-15</sup> nickel<sup>16,17</sup> and cobalt.<sup>16,17</sup> They are characterized by

short M-S distances (2.03–2.20 Å) and M-S-M angles ( $157.2$ – $180^\circ$ ) consistent with metal-sulfur  $\sigma$  and  $d\pi$ - $p\pi$  bonding. Theoretical treatments of this bonding have been presented.<sup>17</sup> Complex **1**, originally reported by Lichtenberger and Hubbard, is the only compound of this type known for tungsten.<sup>13</sup> It is a minor product in the reaction of  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_3]^-$  and  $\text{N}_3\text{S}_3\text{Cl}_3$ ; infrared and proton NMR data only were reported. Highly reactive  $[\{\text{W}(\text{CO})_3\}_2(\mu\text{-S})]^{2-}$  is formed upon deprotonation of  $[\{\text{W}(\text{CO})_3\}_2(\mu\text{-SH})]^-$  and can be trapped by reaction with halo compounds; the thio complex was not isolated but was characterized by solution infrared spectroscopy and derivative chemistry.<sup>18</sup> Its structure remains unknown. The only other ( $\mu$ -thio)ditungsten carbonyl complex known is  $[\text{CpW}(\text{CO})_3]_2(\mu\text{-S})$ , which is formed in the reaction of  $\text{CpWH}(\text{CO})_3$  and  $\text{SO}_2$ .<sup>19</sup> A crystal structure of this material revealed that the W-S-W bridge is bent ( $\text{W-S-W} = 127.0(2)^\circ$ ) with W-S distances of 2.531(11) Å.

### Experimental Section

**Materials and Methods.** Propylene sulfide was purchased from Aldrich Chemical Co. 1,2-Dichloroethane was dried ( $\text{P}_2\text{O}_5$ ) and deoxygenated before use, and all reactions were performed under an atmosphere of dinitrogen. Solid state (KBr disk) and solution ( $\text{CH}_2\text{Cl}_2$ ) infrared spectra were recorded on a Jasco A-302 spectrophotometer. Proton NMR spectra ( $\text{CDCl}_3$ ) were obtained using JEOL GX-400 and Varian 300-MHz FT NMR spectrometers. Electron impact (70 eV) mass spectra were recorded on a VG-TRIO-1 mass spectrometer. UV-visible spectra were recorded

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on an Hitachi 150-20 spectrophotometer. Microanalyses were performed by Atlantic Microlabs Inc., Norcross, GA.

**Syntheses.** {HB(Me<sub>2</sub>pz)<sub>3</sub>}WBr(CO)<sub>2</sub>. A suspension of {HB(Me<sub>2</sub>pz)<sub>3</sub>}WBr(CO)<sub>2</sub><sup>20</sup> (0.35 g, 0.543 mmol) in acetonitrile (4 mL) was heated at 70 °C for 30 min. The dark brown precipitate was then filtered off and washed with cold acetonitrile (2 × 5 mL), yield 0.23 g, 69%.

1. A solution of {HB(Me<sub>2</sub>pz)<sub>3</sub>}WBr(CO)<sub>2</sub> (0.16 g, 0.26 mmol) in 1,2-dichloroethane (5 mL) was treated with propylene sulfide (0.03 mL, 0.38 mmol) and refluxed for 2 h. The dark green solution was then reduced to dryness and column chromatographed (silica/dichloromethane), collecting the green fraction which was recrystallized from dichloromethane/pentane to give the blue-green crystalline product, yield 0.05 g, 35%.

An alternative synthesis involved a suspension of {HB(Me<sub>2</sub>pz)<sub>3</sub>}WH(CO)<sub>3</sub><sup>21</sup> (0.5 g, 0.88 mmol) in dichloroethane (30 mL) treated with propylene sulfide (0.15 mL, 1.91 mmol) and refluxed for 4 h. The solution was then reduced to dryness and column chromatographed (silica/dichloromethane). The green fraction was collected and reduced to dryness, and the residue was recrystallized from dichloromethane/pentane to give the blue-green crystalline product, yield 0.34 g, 70%.

Anal. Calcd for C<sub>34</sub>H<sub>44</sub>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub>SW<sub>2</sub>: C, 36.92; H, 4.01; N, 15.19; S, 2.90. Found: C, 36.64; H, 3.94; N, 15.10; S, 2.96. IR spectrum (KBr; cm<sup>-1</sup>): ν(BH) 2550 m; ν(CO) 1960 s, 1880 s, 1865 s, 1845 s; ν(CN) 1540 m; ν(WSW) 600 w. IR spectrum (CH<sub>2</sub>Cl<sub>2</sub>; cm<sup>-1</sup>): ν(CO) 1960 s, 1900 s, 1860 s, 1835 s. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>): δ 2.27 (s, 6H, 2CH<sub>3</sub>), 2.29 (s, 6H, 2CH<sub>3</sub>), 2.3 (br, 12H, 4CH<sub>3</sub>), 2.42 (s, 12H, 4CH<sub>3</sub>), 5.64 (s, 2H, 2CH), 5.77 (br s, 4H, 4CH). Mass spectrum, *m/z* (%) for parent ion: 1100 (1), 1101 (9), 1102 (31), 1103 (52), 1104 (77), 1105 (80), 1106 (100), 1107 (78), 1108 (72), 1109 (36), 1110 (31), 1111 (11), 1112 (3). Electronic spectrum (CH<sub>2</sub>Cl<sub>2</sub>): 580 (1200), 405 nm (ε 1.27 × 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>).

2. A suspension of {HB(Pr<sup>i</sup>pz)<sub>3</sub>}WH(CO)<sub>3</sub><sup>21</sup> (0.3 g, 0.57 mmol) in 1,2-dichloroethane (20 mL) was treated with propylene sulfide (0.1 mL, 1.28 mmol) and refluxed for 5 days. The reaction mixture was reduced to dryness, column chromatographed (silica/dichloromethane), and recrystallized from dichloromethane/pentane to give the dark green crystalline product, yield 0.17 g, 50%.

Anal. Calcd for C<sub>40</sub>H<sub>56</sub>B<sub>2</sub>N<sub>12</sub>O<sub>4</sub>SW<sub>2</sub>: C, 40.36; H, 4.74; N, 14.12; S, 2.69. Found: C, 40.42; H, 4.71; N, 14.06; S, 2.62. IR spectrum (KBr; cm<sup>-1</sup>): ν(BH) 2550 m; ν(CO) 1970 s, 1905 s, 1865 s, 1850 s; ν(CN) 1500 m; ν(WSW) 600 w. IR spectrum (CH<sub>2</sub>Cl<sub>2</sub>; cm<sup>-1</sup>): ν(CO) 1975 s, 1910 s, 1870 s, 1850 s. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -0.33, 0.88, 1.11, 1.18, 1.22, 1.43 (d, *J* = 7.0 Hz, 6 × 6H, 6 × 2CH<sub>3</sub>), 3.39, 3.47, 3.91 (septets, 3 × 2H, 3 × 2CHMe<sub>2</sub>), 5.87, 5.88, 6.23 (d, 3 × 2H, 3 × 2CH), 7.39, 7.46, 7.60 (d, 3 × 2H, 3 × 2CH). Mass spectrum, *m/z* (%) for parent ion: 1186 (12), 1188 (60), 1190 (76), 1191 (83), 1192 (100), 1193 (83), 1194 (73), 1195 (41), 1196 (35), 1197 (13), 1198 (7).

**Crystallography.** Crystals of 1 and 2 were grown by slow diffusion of pentane into dichloromethane solutions of the complexes. Intensity data for blue-green crystals of 1 and 2 were measured on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å; the  $\omega:2\theta$  scan technique was employed to measure data up to a maximum Bragg angle of 27.5° in each case. The data sets were corrected for Lorentz and polarization effects,<sup>22</sup> and an empirical absorption correction was applied.<sup>23</sup> Relevant crystal data are given in Table 1.

The structures were solved by direct methods<sup>24</sup> and refined by a full-matrix least-squares procedure based on *F*.<sup>22</sup> Non-H atoms were refined with anisotropic thermal parameters, and H atoms were included in the models in their calculated positions (C-H, B-H = 0.97 Å). The refinements were continued until convergence by employing  $\sigma$  weights; the analysis of variance showed no special features, indicating that an appropriate weighting scheme had been applied in both cases. The absolute configuration of 2 was determined on the basis of the differences in the Friedel pairs included in the data set. Fractional atomic coordinates are listed in Tables 2 and 3, and the numbering schemes employed are shown

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Table 1. Crystallographic Data

|   | compd   |   |
|---|---|---|
|   | 1   | 2   |
| formula   | C <sub>34</sub> H <sub>44</sub> B <sub>2</sub> N <sub>12</sub> O <sub>4</sub> SW <sub>2</sub> | C <sub>40</sub> H <sub>56</sub> B <sub>2</sub> N <sub>12</sub> O <sub>4</sub> SW <sub>2</sub> |
| cryst size, mm  | 0.08 × 0.19 × 0.23  | 0.25 × 0.25 × 0.25  |
| cryst syst  | monoclinic  | monoclinic  |
| space group   | C2/c  | P2 <sub>1</sub>   |
| <i>a</i> , Å  | 20.315(5)   | 11.433(5)   |
| <i>b</i> , Å  | 14.450(3)   | 14.354(7)   |
| <i>c</i> , Å  | 13.796(2)   | 15.058(4)   |
| $\beta$ , deg   | 103.02(2)   | 103.98(3)   |
| <i>V</i> , Å <sup>3</sup>                                       | 3945(1)   | 2397(1)   |
| <i>Z</i>  | 4   | 2   |
| $\rho_{\text{calcd}}$ , g cm <sup>-3</sup>                      | 1.862   | 1.649   |
| <i>F</i> (000)  | 2152  | 1172  |
| $\mu$ , cm <sup>-1</sup>  | 59.40   | 48.94   |
| transm coeffs   | 0.921–1.226   | 0.943–1.028   |
| data collcd   | + <i>h</i> , + <i>k</i> , ± <i>l</i>  | + <i>h</i> , + <i>k</i> , ± <i>l</i>  |
| no. of data collcd  | 5039  | 4820  |
| no. of unique data  | 4904  | 4578  |
| no. of unique data<br>with <i>I</i> ≥ 3.0 $\sigma$ ( <i>I</i> ) | 3290  | 4245  |
| <i>R</i>  | 0.027   | 0.024   |
| <i>R</i> <sub>w</sub>   | 0.030   | 0.027   |
| residual density, e Å <sup>-3</sup>                             | 0.50  | 0.55  |

Table 2. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 1

| atom              | <i>x</i>   | <i>y</i>   | <i>z</i>   |
|-------------------|------------|------------|------------|
| W(1)              | 0.05129(1) | 0.76919(2) | 0.12758(2) |
| S(1) <sup>a</sup> | 0          | 0.7802(1)  | 1/4        |
| O(1)              | -0.0819(2) | 0.8028(4)  | -0.0274(4) |
| O(2)              | 0.0610(3)  | 0.9825(4)  | 0.1164(5)  |
| N(11)             | 0.1078(2)  | 0.7425(4)  | 0.0151(4)  |
| N(12)             | 0.1554(2)  | 0.6734(3)  | 0.0288(3)  |
| N(21)             | 0.0444(2)  | 0.6177(3)  | 0.1226(4)  |
| N(22)             | 0.1014(3)  | 0.5653(3)  | 0.1269(4)  |
| N(31)             | 0.1520(2)  | 0.7473(3)  | 0.2272(3)  |
| N(32)             | 0.1899(2)  | 0.6723(3)  | 0.2135(3)  |
| C(1)              | -0.0325(3) | 0.7894(4)  | 0.0294(5)  |
| C(2)              | 0.0595(3)  | 0.9032(5)  | 0.1209(5)  |
| C(11)             | 0.0641(4)  | 0.8598(6)  | -0.1155(6) |
| C(12)             | 0.1075(3)  | 0.7815(5)  | -0.0737(5) |
| C(13)             | 0.1548(4)  | 0.7346(5)  | -0.1149(5) |
| C(14)             | 0.1841(3)  | 0.6687(5)  | -0.0481(5) |
| C(15)             | 0.2383(4)  | 0.6024(5)  | -0.0560(6) |
| C(21)             | -0.0759(3) | 0.5855(5)  | 0.1207(5)  |
| C(22)             | -0.0056(3) | 0.5572(4)  | 0.1246(4)  |
| C(23)             | 0.0205(4)  | 0.4682(5)  | 0.1321(5)  |
| C(24)             | 0.0878(3)  | 0.4753(5)  | 0.1340(4)  |
| C(25)             | 0.1396(4)  | 0.4023(5)  | 0.1460(5)  |
| C(31)             | 0.1611(3)  | 0.8744(5)  | 0.3497(5)  |
| C(32)             | 0.1843(3)  | 0.7875(4)  | 0.3118(4)  |
| C(33)             | 0.2414(3)  | 0.7360(5)  | 0.3513(4)  |
| C(34)             | 0.2440(3)  | 0.6647(4)  | 0.2889(4)  |
| C(35)             | 0.2947(3)  | 0.5909(5)  | 0.2957(5)  |
| B(1)              | 0.1675(4)  | 0.6137(5)  | 0.1221(5)  |

<sup>a</sup> Atom has a site occupancy factor = 0.5.

in Figures 1 and 2 (drawn with ORTEP<sup>25</sup> at 30% probability ellipsoids). Selected bond distances and angles are given in Table 4. The teXsan<sup>22</sup> package, installed on an Iris Indigo workstation, was employed for all calculations.

## Results and Discussion

**Syntheses and Spectroscopic Properties.** Reactions 1 and 2 (L = tris(pyrazolyl)borate ligand, [S] and [E] = atom donor



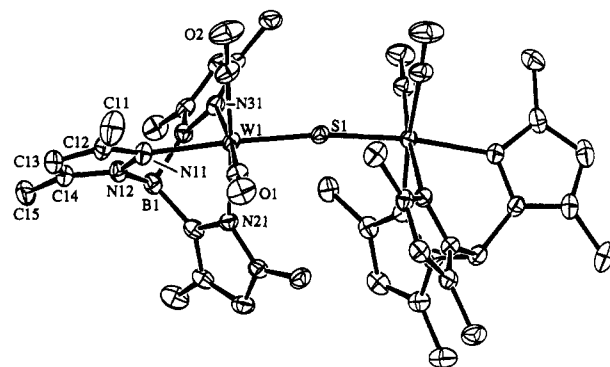
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**Table 3.** Fractional Atomic Coordinates and Their Estimated Standard Deviations for 2

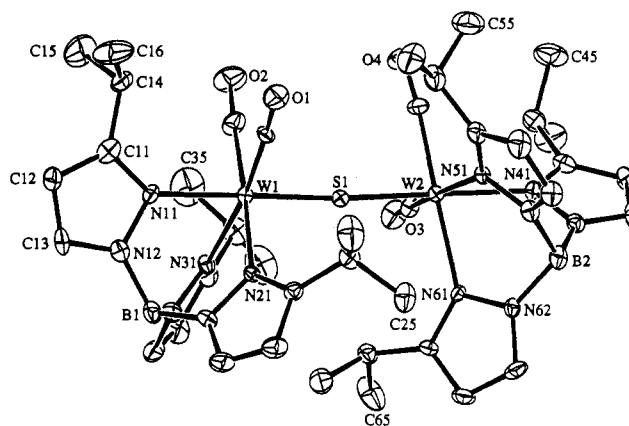
| atom  | x           | y           | z           |
|-------|-------------|-------------|-------------|
| W(1)  | 0.23881(3)  | 0.0320      | 0.06611(2)  |
| W(2)  | 0.49436(3)  | 0.00704(4)  | 0.33108(2)  |
| S(1)  | 0.3602(2)   | 0.0185(5)   | 0.2009(2)   |
| O(1)  | 0.3065(8)   | 0.2369(7)   | 0.0570(6)   |
| O(2)  | 0.4606(6)   | 0.0024(8)   | -0.0144(5)  |
| O(3)  | 0.5561(8)   | -0.1938(6)  | 0.2857(6)   |
| O(4)  | 0.6781(6)   | 0.0478(8)   | 0.2157(5)   |
| N(11) | 0.1146(7)   | 0.0467(10)  | -0.0660(5)  |
| N(12) | -0.0002(6)  | 0.0073(6)   | -0.0795(5)  |
| N(21) | 0.0757(6)   | 0.0636(5)   | 0.1154(5)   |
| N(22) | -0.0293(6)  | 0.0182(7)   | 0.0767(5)   |
| N(31) | 0.1701(7)   | -0.1116(6)  | 0.0487(5)   |
| N(32) | 0.0490(7)   | -0.1265(6)  | 0.0257(5)   |
| N(41) | 0.6249(6)   | -0.0018(10) | 0.4631(4)   |
| N(42) | 0.5922(6)   | 0.0298(6)   | 0.5399(4)   |
| N(51) | 0.4801(7)   | 0.1484(5)   | 0.3843(5)   |
| N(52) | 0.4611(7)   | 0.1594(6)   | 0.4690(5)   |
| N(61) | 0.3656(7)   | -0.0351(6)  | 0.4134(5)   |
| N(62) | 0.3723(6)   | 0.0073(6)   | 0.4952(4)   |
| C(1)  | 0.2819(9)   | 0.1590(8)   | 0.0628(7)   |
| C(2)  | 0.3762(8)   | 0.0095(10)  | 0.0137(6)   |
| C(3)  | 0.5306(9)   | -0.1168(7)  | 0.3031(6)   |
| C(4)  | 0.6137(8)   | 0.0369(9)   | 0.2616(6)   |
| C(11) | 0.1145(10)  | 0.0859(8)   | -0.1470(7)  |
| C(12) | 0.0038(10)  | 0.0738(9)   | -0.2095(7)  |
| C(13) | -0.0651(8)  | 0.0237(10)  | -0.1642(6)  |
| C(14) | 0.2239(10)  | 0.1351(9)   | -0.1648(7)  |
| C(15) | 0.2670(13)  | 0.0872(14)  | -0.2372(10) |
| C(16) | 0.1932(14)  | 0.2349(12)  | -0.1925(11) |
| C(21) | 0.0525(8)   | 0.1189(7)   | 0.1824(6)   |
| C(22) | -0.0675(10) | 0.1073(9)   | 0.1845(8)   |
| C(23) | -0.1139(8)  | 0.0467(10)  | 0.1185(7)   |
| C(24) | 0.1393(10)  | 0.1783(8)   | 0.2420(7)   |
| C(25) | 0.1507(11)  | 0.1529(9)   | 0.3393(8)   |
| C(26) | 0.1078(14)  | 0.2810(9)   | 0.2300(10)  |
| C(31) | 0.2163(11)  | -0.1990(9)  | 0.0571(7)   |
| C(32) | 0.1282(12)  | -0.2644(8)  | 0.0423(8)   |
| C(33) | 0.0225(12)  | -0.2161(8)  | 0.0211(7)   |
| C(34) | 0.3484(12)  | -0.2170(9)  | 0.0734(10)  |
| C(35) | 0.3790(14)  | -0.2251(12) | -0.0161(11) |
| C(36) | 0.3822(13)  | -0.3045(10) | 0.1276(11)  |
| C(41) | 0.7395(9)   | -0.0340(8)  | 0.4945(8)   |
| C(42) | 0.7767(9)   | -0.0227(9)  | 0.5868(7)   |
| C(43) | 0.6849(8)   | 0.0185(9)   | 0.6136(6)   |
| C(44) | 0.8097(9)   | -0.0707(9)  | 0.4309(8)   |
| C(45) | 0.8995(10)  | 0.0007(13)  | 0.4195(9)   |
| C(46) | 0.8661(11)  | -0.1602(10) | 0.4631(9)   |
| C(51) | 0.4843(10)  | 0.2362(8)   | 0.3536(7)   |
| C(52) | 0.4690(11)  | 0.2966(9)   | 0.4181(8)   |
| C(53) | 0.4537(9)   | 0.2478(8)   | 0.4893(8)   |
| C(54) | 0.5193(12)  | 0.2588(8)   | 0.2671(9)   |
| C(55) | 0.6597(13)  | 0.2650(11)  | 0.2856(10)  |
| C(56) | 0.4605(14)  | 0.3479(9)   | 0.2240(9)   |
| C(61) | 0.2735(8)   | -0.0953(7)  | 0.4008(7)   |
| C(62) | 0.2221(9)   | -0.0913(8)  | 0.4737(7)   |
| C(63) | 0.2862(9)   | -0.0267(8)  | 0.5325(7)   |
| C(64) | 0.2353(9)   | -0.1573(8)  | 0.3199(7)   |
| C(65) | 0.2416(12)  | -0.2585(9)  | 0.3462(9)   |
| C(66) | 0.1102(12)  | -0.1337(9)  | 0.2693(9)   |
| B(1)  | -0.0357(11) | -0.0459(9)  | -0.0026(8)  |
| B(2)  | 0.4702(11)  | 0.0775(8)   | 0.5325(8)   |

reagent) offer an alternative approach to compounds such as  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WOSCl}$  and  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WS}_2\text{Cl}$ . However, reaction 1 does not take place when  $n$  is greater than one.<sup>26</sup> Instead, reaction of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WBr}(\text{CO})_2$  or  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WH}(\text{CO})_3$  with propylene sulfide in refluxing 1,2-dichloroethane results in good yields of blue, air-stable, diamagnetic 1; the reactions, which may be conveniently monitored by thin-layer chromatography (silica/dichloromethane) or solution infrared spectroscopy, pro-

(26) The  $\pi^2$ -acetonitrile complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WI}(\text{CO})(\text{MeCN})$  has been prepared and reacts with propylene sulfide to give high yields of the thio carbonyl complex  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{WSI}(\text{CO})$ : Thomas, S.; Young, C. G. Unpublished results.



**Figure 1.** Molecular structure and crystallographic numbering scheme for 1. The numbering of atoms in the rings containing N(21) and N(31) parallels that shown for the ring containing N(11). Carbonyl O( $n$ ) atoms are bonded to C( $n$ ) atoms.



**Figure 2.** Molecular structure and crystallographic numbering scheme for 2. The numbering of atoms in the rings containing N(21)–N(61) parallels that shown for the ring containing N(11). Carbonyl O( $n$ ) atoms are bonded to C( $n$ ) atoms.

ceed at appreciable rates only above *ca.* 80 °C. A similar reaction takes place when complexes of the bulkier hydrotris(3-isopropylpyrazolyl)borate are reacted with propylene sulfide, producing blue, diamagnetic air-stable 2. The complexes are intensely colored and are soluble and stable for long periods in chlorinated solvents, acetonitrile, and tetrahydrofuran. They are insoluble in methanol and hydrocarbon solvents. Extension of our syntheses for 1 and 2 may provide reliable, high-yield syntheses for related  $[\text{MSM}]^{n+}$  complexes and thereby assist the development of the chemistry of this class of compound. Complexes 1 and 2 may also be isolated upon (1) reaction of  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{W}(\text{CO})_3$ <sup>27</sup> and propylene sulfide (35% yield, *cf.* ref 15), (2) reaction of  $\text{NEt}_4[\text{LW}(\text{CO})_3]$ <sup>21,28</sup> with propylene sulfide (*ca.* 20%), and (3) reaction of  $\text{NEt}_4[\text{LW}(\text{CO})_3]$  with  $\{(\text{Pr}^i\text{O})_2\text{P}(\text{S})\text{S}\}_2$  (15%).

Analytical data and mass spectra were consistent with the formulation  $[\text{LW}(\text{CO})_2]_2(\mu\text{-S})$  for 1 and 2. The observation of strong parent ions in the mass spectra of 1 and 2 is consistent with the maintenance of the binuclear structure in the gas phase. The mass spectrum of 1 exhibits strong clusters at  $m/z$  1106 (25%),  $[\text{M}]^+$ , and 994 (100%),  $[\text{M} - 4\text{CO}]^+$ . The mass spectrum of 2 exhibits strong clusters of peaks at 1192 (34%),  $[\text{M}]^+$ , 1106 (20%),  $[\text{M} - 3\text{CO}]^+$ , and 1078 (75%),  $[\text{M} - 4\text{CO}]^+$  (100% at  $m/z$  55).

Solution (dichloromethane) and solid-state (KBr) infrared spectra reveal the presence of four  $\nu(\text{CO})$  bands in both compounds. Group theoretical considerations of the allowed  $\nu(\text{CO})$  bands for ideal  $C_2$ ,  $C_{2v}$ , and  $C_{2h}$  isomers of  $[\text{LW}(\text{CO})_2]_2(\mu\text{-S})$  reveal that four, three, and two bands, respectively, are predicted for complexes with these symmetries. The presence of

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Table 4. Comparison of Bond Distances (Å) and Bond Angles (deg) for 1 and 2

| 1                |           | 2                |          | 2                |          |
|------------------|-----------|------------------|----------|------------------|----------|
| W(1)–S(1)        | 2.1809(3) | W(1)–S(1)        | 2.173(3) | W(2)–S(1)        | 2.184(3) |
| W(1)–C(1)        | 1.944(6)  | W(1)–C(1)        | 1.89(1)  | W(2)–C(3)        | 1.90(1)  |
| W(1)–C(2)        | 1.947(7)  | W(1)–C(2)        | 1.948(9) | W(2)–C(4)        | 1.957(8) |
| W(1)–N(11)       | 2.163(5)  | W(1)–N(11)       | 2.157(7) | W(2)–N(41)       | 2.182(7) |
| W(1)–N(21)       | 1.194(5)  | W(1)–N(21)       | 2.214(7) | W(2)–N(61)       | 2.226(7) |
| W(1)–N(31)       | 2.163(5)  | W(1)–N(31)       | 2.198(8) | W(2)–N(51)       | 2.202(7) |
| C(1)–O(1)        | 1.143(7)  | C(1)–O(1)        | 1.16(1)  | C(3)–O(3)        | 1.19(1)  |
| C(2)–O(2)        | 1.149(7)  | C(2)–O(2)        | 1.15(1)  | C(4)–O(4)        | 1.13(1)  |
| W(1)–S(1)–W(1')  | 171.6(1)  | W(1)–S(1)–W(2)   | 175.3(1) | C(3)–W(2)–S(1)   | 90.9(3)  |
| C(1)–W(1)–S(1)   | 91.9(2)   | C(1)–W(1)–S(1)   | 89.9(3)  | C(3)–W(2)–C(4)   | 82.4(5)  |
| C(1)–W(1)–C(2)   | 83.6(3)   | C(1)–W(1)–C(2)   | 84.8(5)  | C(3)–W(2)–N(41)  | 90.5(5)  |
| C(1)–W(1)–N(11)  | 92.8(2)   | C(1)–W(1)–N(11)  | 89.9(5)  | C(3)–W(2)–N(61)  | 94.5(4)  |
| C(1)–W(1)–N(21)  | 95.0(2)   | C(1)–W(1)–N(21)  | 93.3(4)  | C(3)–W(2)–N(51)  | 169.9(3) |
| C(1)–W(1)–N(31)  | 174.3(2)  | C(1)–W(1)–N(31)  | 171.0(4) | C(4)–W(2)–S(1)   | 86.1(3)  |
| C(2)–W(1)–S(1)   | 91.4(2)   | C(2)–W(1)–S(1)   | 88.2(3)  | C(4)–W(2)–N(41)  | 95.1(3)  |
| C(2)–W(1)–N(11)  | 95.4(2)   | C(2)–W(1)–N(11)  | 93.3(3)  | C(4)–W(2)–N(61)  | 176.3(4) |
| C(2)–W(1)–N(21)  | 175.0(2)  | C(2)–W(1)–N(21)  | 175.4(4) | C(4)–W(2)–N(51)  | 96.9(4)  |
| C(2)–W(1)–N(31)  | 95.4(2)   | C(2)–W(1)–N(31)  | 95.5(5)  | N(41)–W(2)–S(1)  | 178.3(3) |
| N(11)–W(1)–S(1)  | 172.8(1)  | N(11)–W(1)–S(1)  | 178.5(3) | N(41)–W(2)–N(61) | 82.8(3)  |
| N(11)–W(1)–N(21) | 80.8(2)   | N(11)–W(1)–N(21) | 82.5(3)  | N(41)–W(2)–N(51) | 79.5(4)  |
| N(11)–W(1)–N(31) | 81.6(2)   | N(11)–W(1)–N(31) | 81.1(4)  | W(2)–C(3)–O(3)   | 178.4(9) |
| W(1)–C(1)–O(1)   | 178.7(6)  | W(1)–C(1)–O(1)   | 177.3(9) | W(2)–C(4)–O(4)   | 174(1)   |
| W(1)–C(2)–O(2)   | 176.6(6)  | W(1)–C(2)–O(2)   | 175(1)   |                  |          |

four bands confirms the prevalence of the  $C_2$  isomer in solution as well as in the solid state, as confirmed by X-ray crystallographic studies. The  $\nu(\text{CO})$  bands reported for **1** closely match those previously reported by Lichtenberger and Hubbard,<sup>13</sup> and four bands are also observed for the related  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_2]_2(\mu\text{-S})$ <sup>14</sup> ( $C_2$ ) and  $[\text{CpCr}(\text{CO})_2]_2(\mu\text{-S})$ <sup>6,7</sup> ( $C_1$ , effective  $C_2$ ) complexes. Evidence for a single isomer of **1** in solution is provided by the similarity of its solution IR spectrum and that of **2**, the <sup>1</sup>H NMR spectrum of which is consistent with a single species of  $C_2$  symmetry (vide infra). A strong band at 600  $\text{cm}^{-1}$  in the KBr spectrum is assigned to the  $\nu_{\text{as}}(\text{W-S-W})$  vibration, consistent with the assignment of a similar band in complexes such as  $[\text{Mo}_2(\mu\text{-S})(\text{CN})_{12}]^{6-9}$  and  $\text{Mo}_2(\mu\text{-S})(\text{S}_2\text{CNET}_2)_6$ .<sup>12</sup>

The <sup>1</sup>H NMR spectrum of **1** has been reported by Lichtenberger and Hubbard;<sup>13</sup> our observations and conclusions are in agreement with theirs. At room temperature, broad (4H) and sharp (2H) CH resonances are observed along with three (12H, 6H, 6H) sharp CH<sub>3</sub> resonances. An extremely broad feature upon which the methyl resonances are superimposed integrates for 12 hydrogens and may be assigned to the remaining methyl groups. The spectrum is consistent with rotation about the W–S bonds on the NMR time scale and effective  $C_2$  symmetry at each tungsten center, as previously described.<sup>13</sup> Molecules such as  $[\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{CO})_2]_2(\mu\text{-S})$ ,<sup>13</sup>  $\text{Mo}_2(\mu\text{-S})(\text{S}_2\text{CNET}_2)_6$ ,<sup>12</sup> and  $[\text{CpCr}(\text{CO})_2]_2(\mu\text{-S})$ <sup>6,7</sup> are also fluxional on the NMR time scale. The crystallographic characterization of eclipsed ( $C_{2v}$ , ideal  $D_{5h}$ )<sup>9</sup> and staggered ( $D_{5d}$ )<sup>10</sup> forms of  $[\text{Mo}_2(\mu\text{-S})(\text{CN})_{12}]^{6-}$  in two different salts supports a small barrier to rotation about the M–S bonds. In contrast, the <sup>1</sup>H NMR spectra of **2** is consistent with a nonfluxional molecule of  $C_2$  symmetry. The six doublet resonances in the  $\delta$  –0.5 to 1.5 region may be assigned to six sets (pairs) of inequivalent methyl groups, the methyl groups of each isopropyl group being diastereotopic in the dissymmetric, chiral molecule. Similarly, the isopropyl CH and ring proton resonances are all inequivalent. The resonance at  $\delta$  –0.33 is considerably shielded with respect to the other methyl resonances, a feature of the spectra of other compounds containing M–S multiple bonds, e.g.  $\{\text{HB}(\text{Me}_2\text{pz})_3\}\text{Mo}(\text{S}_4)\text{Cl}$ .<sup>29</sup> The interlocking of the bulky isopropyl groups of **2** (vide infra) effectively prevents relative motion of the two LW(CO)<sub>2</sub> fragments in this molecule.

Complex **1** exhibits strong absorptions around 580 ( $\epsilon$  1200  $\text{M}^{-1} \text{cm}^{-1}$ ) and 400 ( $\epsilon$   $1.27 \times 10^5 \text{M}^{-1} \text{cm}^{-1}$ ) nm due to charge-

transfer transitions. The low-energy band is unsymmetrical concealing a weak band with an estimated wavelength of 630 nm. Similar spectra have been reported for  $[\{\text{HBpz}_3\}\text{Mo}(\text{CO})_2]_2(\mu\text{-S})$ <sup>14</sup> and  $[\text{Mo}_2(\text{S}(\text{CN})_{12})]^{6-,8,9,11}$

**Description of Structures.** The unit cells of **1** and **2** contain the discrete binuclear molecules shown in Figures 1 and 2, respectively. Selected bond distances and angles are given in Table 4. The tungsten centers possess distorted octahedral geometries, defined by the coordination of two terminal carbonyl ligands, a facially tridentate pyrazolylborate ligand, and a single bridging thio ligand. The S(1) atom of complex **1** is situated on a crystallographic 2-fold symmetry axis, and the molecule possesses  $C_2$  symmetry. There is no crystallographic symmetry imposed on molecules of **2**, but they closely approximate  $C_2$  symmetry. The triatomic  $[\text{W}_2\text{S}]^{2+}$  linkages are characterized by short W–S distances (2.1809(3) Å for **1**, 2.173(3) and 2.184(3) Å for **2**) and nearly linear W–S–W bond angles (171.6(1)° for **1** and 175.3(1)° for **2**). These distances are much shorter than those observed in all other W–( $\mu\text{-S}$ )–W compounds, i.e. ca. 2.3–2.6 Å.<sup>19,30–33</sup> Likewise, the W–S–W angles are much larger than those previously reported (ca. 90–130°).<sup>19,30–33</sup> The only other structurally characterized ( $\mu$ -thio)ditungsten complex,  $[\text{CpW}(\text{CO})_2]_2(\mu\text{-S})$ , has a bent W–S–W bridge (W–S–W = 127.0(2)°) and much longer W–S distances of average 2.531 Å.<sup>19</sup> In the non-carbonyl complexes,  $[\text{W}_2\text{E}_2(\text{S}_2)_4(\mu\text{-S})]^{2-}$  (E = O, S), the respective W–( $\mu\text{-S}$ ) distances and W–S–W bond angles are 2.534(4) Å, 90.0(2)° and 2.461(2) Å, 90.5(1)°.<sup>33</sup> In fact, the W–S distances in **1** and **2** are only slightly longer than W=S distances typical of multiply bonded terminal thio ligand complexes of  $\text{W}^{\text{VI}}\text{W}^{\text{IV}}$ , where an average W=S distance of 2.115 Å pertains.<sup>30–35</sup> The W–S distances of **1** and **2** are therefore consistent with considerable multiple-bond character within the  $[\text{W}_2\text{S}]^{2+}$  fragment. For the molybdenum analogue of **1**, an Mo–S distance of 2.200(2) Å and an Mo–S–Mo angle of 171.5(4)° were reported by Enemark *et al.*<sup>14</sup>

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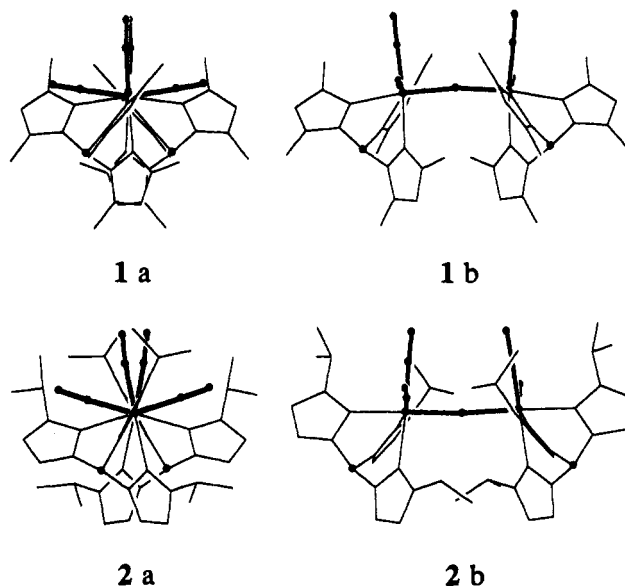
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The shortest W–N distances in both molecules involve the axial nitrogen donors N(11) and N(41), but the range of W–N distances (2.163(5)–2.226(7) Å) is relatively small compared to Mo and W complexes possessing terminal thio ligands.<sup>35a,36</sup> In these complexes, the M–N bond *trans* to the multiple bond is up to 0.26 Å longer than the others, in contrast to the observations for **1** and **2**. The major distortions from octahedral geometry result from the constraint of N–W–N angles to less than 90° (79.5(4)–86.1(3)°) in the tripodal pyrazolylborate ligands and the average 83.6° C–W–C angles. Similar trends in the M–N distances are observed for related [MoSMo]<sup>2+</sup> complexes.<sup>14</sup>

Other structural differences are related to the steric interactions of the pyrazolylborate substituents. Views along and across the W...W vector of **1** and **2**, shown in Figure 3, clearly reveal these structural differences. For **1**, the dihedral angle relating the *syn*-carbonyl ligands (C(2)–W(1)–W(1')–C(2')) = 4.9(2)° is smaller than the corresponding dihedral angle in **2** (C(2)–W(1)–W(2)–C(4)) = 21.5(6)° (views **1a** and **2a**). As the C–W–C angles in both complexes are very similar, there is a consequent difference in the dihedral angle relating the *anti*-carbonyl ligands in both complexes (162.7(3)° for **1** and 145.7(5)° for **2**). In **1**, the *syn*-carbonyl ligands are inclined away from one another and the thio ligand resides on the same side of the W...W vector as these carbonyl ligands (view **1b**). For **2**, the disposition of the bridging sulfur atom and *syn* carbonyl ligands with respect to the W...W vector leads to the inclination of the *syn*-carbonyl ligands toward one another. The S–W–C angles range from 91.9(2) to 86.1(3)°. Four of the isopropyl substituents in **2** are interlocked



**Figure 3.** Views of **1** and **2** (a) along and (b) across (perpendicular to) the W...W vector. The [(CO)<sub>2</sub>WSW(CO)<sub>2</sub>]<sup>2+</sup> core and boron atoms are highlighted, and for clarity only the outlines of the pyrazole rings are shown.

around the girdle of the complex accounting for the stereochemical rigidity of the molecule revealed by NMR. Steric congestion in this region accounts for the greater distortion of **2** relative to **1**. A 1,2-borotropic shift, induced by unfavorable steric interactions in other systems featuring the HB(Pr<sup>i</sup>pz)<sub>3</sub><sup>-</sup> ligand,<sup>37,38</sup> is not observed in **2**. The closest intermolecular non-hydrogen contact for **1** involves O(2) and C(35) (3.305(8) Å) and for **2** involves O(4) and O(22) (3.08(1) Å).

The bonding in [MSM]<sup>+</sup> complexes has been discussed, and molecular orbital treatments for [[Ni(PH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>(μ-S)]<sup>2+</sup>,<sup>17</sup> [[Cr(CO)<sub>3</sub>](μ-S)]<sup>2+</sup>,<sup>17</sup> and [CpCr(CO)<sub>2</sub>]<sub>2</sub>(μ-S)<sup>39</sup> have been presented. σ-Bonds result from the interaction of the two sp hybrid orbitals on sulfur and the metal d<sub>z</sub> orbitals (z along MSM). As well, the interaction of metal d<sub>xx</sub> and d<sub>yz</sub> orbitals and sulfur p<sub>x</sub> and p<sub>y</sub> orbitals produces dπ–pπ orbitals which fall into three groups: a pair of bonding orbitals, a pair of nonbonding orbitals, and a pair of antibonding orbitals. As for [[HB(Me<sub>2</sub>pz)<sub>3</sub>Mo(CO)<sub>2</sub>](μ-S)],<sup>14</sup> σ- and π-bonding and π-nonbonding orbitals are fully occupied in the 16-electron ditungsten complexes **1** and **2**. A nonbonding orbital on each tungsten atom is also fully occupied thereby permitting the stabilization of the π-acid carbonyl ligands.

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**Supplementary Material Available:** Listings of thermal parameters, H atom parameters, and all bond distances and angles (14 pages). Ordering information is given on any current masthead page.

- (35) Other examples (with W=S distance in Å) include the following: (a) {HB(Me<sub>2</sub>pz)<sub>3</sub>}WS(S<sub>2</sub>CNEt<sub>2</sub>), 2.153(2); Young, C. G.; Bruck, M. A.; Enemark, J. H. *Inorg. Chem.* **1992**, *31*, 593. (b) WSCl<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>, 2.101(5); Fedin, V. P.; Mironov, Y. V.; Virovets, A. V.; Podbereskaya, N. V.; Fedorov, V. Y.; Semyannikov, P. P. *Polyhedron* **1992**, *11*, 279. (c) WSCl<sub>4</sub>, 2.08(1); Cotton, F. A.; Kibala, P. A.; Sandor, R. B. W. *Inorg. Chem.* **1989**, *28*, 2485. (d) [WS(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>]<sup>+</sup>, 2.127(2); Snow, M. R.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chim. Acta* **1988**, *150*, 161. (e) [WOS(NCS)<sub>4</sub>]<sup>2-</sup>, 2.108(2); Potvin, C.; Manoli, J. M.; Marzak, S.; Secheresse, F. *Acta Crystallogr., Sect. C* **1988**, *44*, 369. (f) [WS(Se<sub>2</sub>)<sub>2</sub>]<sup>2-</sup>, 2.011(4); Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790. (g) WS(O<sup>i</sup>Bu)<sub>4</sub>, 2.140(1); Chisholm, M. H.; Huffman, J. C.; Pasterczyk, J. W. *Polyhedron* **1987**, *6*, 1551. (h) W<sub>2</sub>S<sub>4</sub>Cl<sub>2</sub>(py)<sub>4</sub>, 2.15; Drew, M. G. B.; Hobson, R. J.; Rice, D. A.; Turp, N. *J. Chem. Soc., Dalton Trans.* **1986**, 2165. (i) WS(S<sub>2</sub>)(S<sub>2</sub>CNBu<sub>2</sub>)<sub>2</sub>, 2.136(1); Pan, W.-H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1985**, 927. (j) WS(S<sub>2</sub>CNEt<sub>2</sub>)(S<sub>2</sub>CNEt<sub>2</sub>)(PhC<sub>2</sub>Ph), 2.138(5); Brower, D. C.; Tonker, T. L.; Morrow, J. R.; Rivers, D. S.; Templeton, J. L. *Organometallics* **1986**, *5*, 1093. (k) WS(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(PhC<sub>2</sub>Ph), 2.147(2); Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745. (l) WSF<sub>4</sub>, 2.104(7); Rice, D. A.; Hagen, K.; Hedberg, L.; Hedberg, K.; Staunton, G. M.; Holloway, J. H. *Inorg. Chem.* **1984**, *23*, 1826. (m) WSCl<sub>4</sub>, 2.086(6); Page, E. M.; Rice, D. A.; Hagen, K.; Hedberg, L.; Hedberg, K. *Inorg. Chem.* **1982**, *21*, 3280. (n) [WSCl<sub>5</sub>]<sup>-</sup>, 2.13(1); Drew, M. G. B.; Fowles, G. W. A.; Page, E. M.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2409. (o) WSCl<sub>3</sub>(MeSCH<sub>2</sub>CH<sub>2</sub>SMe), 2.146; Drew, M. G. B.; Griffin, G. F.; Rice, D. A. *Inorg. Chim. Acta* **1979**, L192. (p) W<sub>2</sub>S<sub>2</sub>Cl<sub>8</sub>(dme), 2.07; Britnell, D.; Drew, M. G. B.; Fowles, G. W. A.; Rice, D. A. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 501. (q) [WSCl<sub>4</sub>]<sub>2</sub>, 2.098(8); and [WSBr<sub>4</sub>]<sub>2</sub>, 2.08(2); Drew, M. G. B.; Mandyczewsky, R. *J. Chem. Soc. A* **1970**, 2815. (r) [WS<sub>4</sub>]<sup>2-</sup>, 2.165; Sasvari, K. *Acta Crystallogr.* **1963**, *16*, 719.
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