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Products of Partial Oxidative Decarbonylation of Tricarbonyl{hydrotris(3,5-dimethyl-1-pyrazolyl)borato}tungstate(0) by Tetraalkylthiuram Disulfides: $\{HB(Me_2C_3N_2H)_3\}W(CO)_2(S_2CNEt_2)$, Mixed-Valence $\{HB(Me_2C_3N_2H)_3\}W^{II}(CO)_2(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(SCNEt_2)$, and Related Complexes

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The synthesis and spectroscopic and X-ray structural characterization of carbonyl complexes $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ (**1**) and mixed-valence $\{HB(Me_2pz)_3\}W^{II}(CO)_2(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(SCNEt_2)$ (**2**) [$HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion] are reported. These complexes are formed as intermediates in the reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ with tetraethylthiuram disulfide, $[S_2CNEt_2]_2$, in acetonitrile at ca. 80 °C; the ultimate products of the reaction are $\{HB(Me_2pz)_3\}WS(S_2CNEt_2)$, $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$, and $[W(S_2CNEt_2)_4]^+$ (see following paper in this issue). Complex **1** ($C_{22}H_{32}BN_7O_2S_2W$) crystallizes in triclinic space group $P\bar{1}$ with $a = 10.201$ (1) Å, $b = 10.172$ (1) Å, $c = 14.937$ (2) Å, $\alpha = 90.00$ (1)°, $\beta = 97.61$ (1)°, $\gamma = 117.89$ (1)°, $V = 1354.4$ Å^3, and $Z = 2$. The seven-coordinate monomer exhibits a distorted pentagonal bipyramidal structure with a carbonyl ligand and one nitrogen donor atom of the $HB(Me_2pz)_3^-$ ligand occupying axial positions; the equatorial plane contains a carbonyl ligand, the bidentate dithiocarbamate ligand, and the two remaining nitrogen donor atoms of the $HB(Me_2pz)_3^-$ ligand. On the basis of analytical and spectroscopic data and a partial crystal structure determination, **2** is proposed to be a dinuclear mixed-valence complex composed of six-coordinate $\{HB(Me_2pz)_3\}W^{II}(CO)_2(\mu\text{-}S)$ and seven-coordinate $(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(SCNEt_2)$ fragments linked by the shared μ-S ligand. The methyl analogues of **1** and **2** form in the analogous reaction using tetramethylthiuram disulfide.

Introduction

Oxidative decarbonylation of metal carbonyl complexes is a ubiquitous reaction in transition-metal organometallic chemistry. Generally, decarbonylation is a consequence of the inability of the metal center to satisfy, upon its oxidation, the electronic requirements of the π-acid carbonyl ligand. In simple cases, the oxidative decarbonylation of metal carbonyls by tetraalkylthiuram disulfides ($[S_2CNR_2]_2 = R_4tds$)[2] is coupled to the reduction of the disulfide (eq 1) and the incorporation of the resultant dithiocarbamate ligands into the metal coordination sphere.

$$[S_2CNR_2]_2 + 2e^- \rightarrow 2S_2CNR_2^- \qquad (1)$$

However, the complexity of reactions involving thiuram disulfides and dithiocarbamates has been evident in many studies. Rarely are these reactions fully described by simple redox (e.g. eq 1) and complexation reactions. Moreover, the course of many reactions is critically dependent upon the conditions under which they are performed. Consider, for example, the reactions of $Mo(CO)_6$,[3] $W(CO)_6$,[3d,4] and $W(CO)_3(MeCN)_3$[5,6] with thiuram disulfides. In the first reaction, a variety of products including $Mo(S_2CNR_2)_4$,[3a] $[Mo(S_2CNR_2)_4]^+$,[3c,d] $Mo_2(S_2CNR_2)_6$,[3b,d] and $Mo_4(\mu_3\text{-}S)_4(S_2CNR_2)_6$[3f,g] may be isolated by changing the conditions of the reaction, particularly the means (thermal or photochemical) of inducing it, a far cry from the simple reaction (eq 2) proposed

$$Mo(CO)_6 + 2R_4tds \rightarrow Mo(S_2CNR_2)_4 + 6CO \qquad (2)$$

in the early account of this reaction.[3a] The second reaction exhibits foibles of a similar nature although a tetranuclear complex has not been reported to form.[4] The third reaction is reported to yield $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$,[5] $W_2(\mu\text{-}S)_2(OMe)_4(S_2CNEt_2)_2$[5] (upon methanol workup), or $W(S_2CNEt_2)_4$.[6] Interestingly, the intermediate carbonyl complexes formed in these reactions have not been identified or, from these reactions at least, isolated. One complicating feature of dithiocarbamate chemistry, exemplified in the formation of $Mo_4(\mu_3\text{-}S)_4(S_2CNR_2)_6$ and $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$ in the reaction above, is the reduction and fragmentation of the dithiocarbamate ligand into species which may be variously stabilized by coordination to the oxidized metal center (eq 3); the formation of thiocarboxamido and thio complexes is

$$S_2CNR_2^- \xrightarrow{2e^-} SCNR_2^- + S^{2-} \qquad (3)$$

most relevant to the present study. Thiocarboxamido complexes are now known for the group 6 elements Mo[7-10] and W,[11-14] Mn,[8,15] and all of the elements of groups 8,[16-21] 9,[14,20,22-26] and 10.[22,27-31]

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The most common synthetic route involves reaction of $ClSCNR_2$ with neutral or anionic metal carbonyls.[7,8,15,17–19,22,24–29] Their synthesis from dithiocarbamate ligands is with one exception[23] restricted to examples involving Mo and W chemistry.[9–14] In 1973, Weiss and co-workers[9] reported the synthesis of $Mo_2(\mu\text{-}S)_2(S_2CNPr^n{}_2)_2(SCNPr^n{}_2)_2$ by reaction of $Mo_2(O_2CMe)_4$ and $NH_4S_2CNPr^n{}_2$, a case where both fragments of the dithiocarbamate ligands are incorporated into the final product. More recently, a variety of organometallic (thiocarboxamido)-molybdenum and -tungsten complexes have been described. These include $Mo_2S(RC_2R)(S_2CNR_2)_3(SCNR_2)$,[10] $W(S_2CNEt_2)(SCNEt_2)(CO)(CHSR)$,[11] and $WS(PhC_2Ph)(S_2CNR_2)(SCNR_2)$[12,13] and WCo_2 cluster complexes.[14] The formation of thio complexes from dithiocarbamates is also well documented but in many cases is not accompanied by the stabilization of the thiocarboxamido fragment.[32]

We have reported the synthesis of the novel complexes $\{HB(Me_2pz)_3\}Mo(\eta^1\text{-}S_2CNR_2)(\eta^2\text{-}S_2CNR_2)$ upon oxidative decarbonylation of $NEt_4[\{HB(Me_2pz)_3\}Mo(CO)_3]$ by R_4tds (R = Me, Et);[33] we were unable to detect or isolate intermediate carbonyl complexes in these reactions. An interest in understanding the course of this type of reaction led us to explore the analogous tungsten system with the expectation that intermediate carbonyl complexes would be stable enough to isolate and characterize. Our investigation of the tungsten system was further encouraged by the likelihood that tungsten would be sufficiently thiophilic to induce the decomposition of $\{HB(Me_2pz)_3\}W(S_2CNR_2)_2$ to thiotungsten species such as $[\{HB(Me_2pz)_3\}WS(S_2CNR_2)]^{0/+}$. The reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ with tetraethylthiuram disulfide in hot acetonitrile yields a number of products depending upon reaction conditions; these may be classified as partially or completely decarbonylated with respect to $[\{HB(Me_2pz)_3\}W(CO)_3]^-$. This contribution describes the products of partial decarbonylation, the seven-coordinate W^{II} complex $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ (**1**), $\{HB(Me_2pz)_3\}W(CO)(S_2CNEt_2)$, and the mixed-valence thiocarboxamido $W^{II}W^{IV}$ complex $\{HB(Me_2pz)_3\}W(CO)_2(\mu\text{-}S)W(S_2CNEt_2)_2(SCNEt_2)$ (**2**). Three products of complete decarbonylation, viz. $\{HB(Me_2pz)_3\}WS(S_2CNEt_2)$, $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$, and $[W(S_2CNEt_2)_4]^+$, are described in the following paper in this issue.[34] Our investigation has revealed many of the nuances of this complex reaction and has provided an insight into the course of the reaction at the molecular level.

Experimental Section

Table I. Crystallographic Data for **1**

chem formula $C_{22}H_{32}BN_7O_2S_2W$	formula mass 685.34
a = 10.201 (1) Å	space group $P\bar{1}$
b = 10.172 (1) Å	T = 23 (1) °C
c = 14.937 (2) Å	λ = 0.71073 Å
α = 90.00 (1)°	ρ_{obsd} = 1.66 g cm^{-3}, ρ_{calcd} = 1.68 g cm^{-3}
β = 97.61 (1)°	μ = 45.4 cm^{-1}
γ = 117.89 (1)°	$R(F_o)$ = 0.037[a]
V = 1354.4 Å^3	$R_w(F_o)$ = 0.050[a]
Z = 2	

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

Materials and Methods. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate and $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ were prepared by methods described by Trofimenko,[35,36] and the thiuram disulfides were purchased from Aldrich Chemical Co. These starting materials were recrystallized from acetonitrile before use. The solvents employed were dried and deoxygenated, and all reactions were performed under an atmosphere of dinitrogen using standard Schlenk line techniques. Control of the reaction temperatures was achieved using a PMC Dataplate Series 720 hotplate/stirrer. No precautions were taken to protect the reactions from normal laboratory fluorescent lighting. Solution (CaF_2 cell) and solid-state (KBr disk) infrared spectra were recorded on a Mattson Polaris FT-IR spectrophotometer calibrated with polystyrene. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-400 MHz spectrometer, and chemical shifts were referenced against the solvent peak. Electron-impact (70 eV) mass spectra were obtained on a VG-7070F double-focus spectrometer with an ion source temperature of 200 °C. Electronic spectra were recorded on a Shimadzu UV-240 visible recording spectrophotometer. Microanalyses were performed by Atlantic Microlabs, Norcross, GA.

Synthesis of Complexes. Complex 1. A mixture of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ (2.0 g, 2.88 mmol) and Et_4tds (1.0 g, 3.37 mmol) in acetonitrile (40 mL) was refluxed for 1 h. Upon cooling, the solvent was evaporated from the reaction mixture and the residue was extracted with ca. 20 mL of dichloromethane. Filtration (to remove unreacted tricarbonyl) followed by slow addition of ca. 200 mL of methanol to the filtrate precipitated the complex as dark brown-black crystals. The yield was 0.75 g (38%). A second crop of product may be obtained by cooling the mother liquor at −4 °C. The combined yield was 0.98 g (50%).

Anal. Calcd for $C_{22}H_{32}BN_7O_2S_2W$: C, 38.56; H, 4.71; N, 14.31; S, 9.36. Found: C, 38.38; H, 4.72; N, 14.31; S, 9.54. Infrared spectrum: (KBr) 2980 w, 2920 w, 2550 w, 1960 s, 1820 sh, 1790 s, 1540 m, 1495 m, 1430 m, 1370 m, 1350 m, 1280 m, 1210 m, 1200 m, 1150 m, 1080 w, 1065 m, 1040 w, 855 w, 810 w, 800 m, 775 m, 690 w cm^{-1}; (CH_2Cl_2) 1950 sh, 1940 s, 1815 s, 1800 sh cm^{-1}. ^1H NMR spectrum ($CDCl_3$, 20 °C): δ 1.24 (t, 6 H, J = 7.2 Hz, 2 × Me of $S_2CNEt_2^-$), 2.37 (s, 9 H, 3 × Me of $HB(Me_2pz)_3^-$), 2.40 (s, 9 H, 3 × Me of $HB(Me_2pz)_3^-$), 3.65 (m (br), 4 H, 2 × CH_2 of $S_2CNEt_2^-$), 5.82 (s, 3 H, 3 × CH of $HB(Me_2pz)_3^-$). Electronic spectrum ($CHCl_3$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 630 (137), 465 (sh, 3800), 433 (5200).

Complex 2. A mixture of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ (2.0 g, 2.88 mmol) and Et_4tds (1.70 g, 5.73 mmol) in acetonitrile (50 mL) was heated at 90 °C for 16 h. The reaction mixture was allowed to cool and then filtered in air to remove green $W_2S_2(S_2CNEt_2)_4$. The filtrate was reduced to dryness on a rotary evaporator, and the residue was dissolved in a minimum amount of dichloromethane. Addition of methanol to this solution precipitated the product as black crystals of the mono(dichloromethane) solvate. Yield: 0.52 g (29%).

Anal. Calcd for $C_{32.78}H_{53.56}BCl_{1.56}N_9O_2S_6W_2$ (viz. **2**·$0.78CH_2Cl_2$): C, 31.96; H, 4.38; N, 10.23; S, 15.61; Cl, 4.49. Found: C, 32.07; H, 4.30; N, 10.33; S, 15.50; Cl, 4.49. Recrystallization from MeCN/MeOH or hot MeCN does not lead to solvent incorporation. Anal. Calcd for $C_{32}H_{52}BN_9O_2S_6W_2$: C, 32.97; H, 4.49; N, 10.81; S, 16.50. Found: C, 33.33; H, 4.46; N, 11.04; S, 16.65. Infrared spectra: (KBr) 2974 m, 2931 m, 2525 w, 1886 s, 1815 s, 1542 m, 1456 s, 1434 s, 1375 m, 1355 m, 1272 m, 1210 m, 1195 m, 1148 m, 1065 w, 1004 w, 855 w, 807 w, 780 w, 695 w, 590 w, 480 w, 470 w cm^{-1}; (CH_2Cl_2) 1890 s, 1814 s cm^{-1}. ^1H NMR: ($CDCl_3$) δ 1.32 (m, 15 H, 5 × CH_2CH_3), 1.43 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 2.41 (s, 6 H, 2 × Me of $HB(Me_2pz)_3^-$), 2.46 (s, 3 H, Me of $HB(Me_2pz)_3^-$), 2.53 (s (br), 6 H, 2 × Me of $HB(Me_2pz)_3^-$), 2.72 (s, 3 H, Me of $HB(Me_2pz)_3^-$), 3.78 (m, 10 H, 5 × CH_2CH_3), 4.00 (9-line, 2 H, CH_2CH_3), 5.30 (s, CH_2Cl_2), 5.62 (s, 1 H, CH of $HB(Me_2pz)_3^-$), 5.79 (s, 1 H, CH of $HB(Me_2pz)_3^-$), 5.81 (s, 1 H, CH of $HB(Me_2pz)_3^-$); (CD_2Cl_2) δ 1.29 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 1.33 (m, 12 H, 4 × CH_2CH_3), 1.42 (t, 3 H, J = 7.2 Hz, CH_2CH_3), 2.36, 2.38, 2.39, 2.42, 2.43, 2.70 (s, 3 H, Me of $HB(Me_2pz)_3^-$), 3.65 (m, 4 H, 2 × CH_2CH_3), 3.80 (m, 6 H, 3 × CH_2CH_3), 4.01 (q, 2 H, CH_2CH_3), 5.70 (s, 1 H, CH

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Table II. Positional and Isotropic Thermal Parameters for **1** (Esd's in Parentheses)[a]

atom	*x*	*y*	*z*	*B*, Å^2
W	0.35846 (2)	0.18488 (2)	0.23437 (2)	1.425 (4)
S1	0.4083 (2)	0.1588 (2)	0.4030 (1)	2.16 (3)
S2	0.5587 (2)	0.4302 (2)	0.3243 (1)	2.45 (3)
C1	0.5399 (6)	0.3420 (6)	0.4227 (4)	1.9 (1)
N2	0.6154 (5)	0.4076 (5)	0.5031 (4)	2.3 (1)
C3	0.5955 (8)	0.3223 (8)	0.5848 (5)	3.2 (2)
C4	0.6868 (9)	0.2395 (9)	0.5937 (7)	5.1 (2)
C5	0.7236 (7)	0.5668 (7)	0.5140 (5)	2.7 (1)
C6	0.8836 (8)	0.597 (1)	0.5107 (8)	4.9 (2)
C40	0.5046 (8)	0.3246 (7)	0.1556 (5)	2.9 (2)
O40	0.5848 (7)	0.3952 (8)	0.1083 (4)	5.4 (2)
C50	0.2411 (7)	0.2849 (7)	0.2375 (5)	2.3 (1)
O50	0.1700 (5)	0.3500 (5)	0.2417 (4)	3.9 (1)
N11	0.1664 (5)	−0.0324 (5)	0.2518 (4)	2.1 (1)
N12	0.1450 (5)	−0.1597 (5)	0.2040 (4)	2.1 (1)
C13	0.0209 (7)	−0.2778 (7)	0.2232 (5)	2.7 (2)
C14	−0.0420 (7)	−0.2302 (7)	0.2826 (5)	3.1 (2)
C15	0.0494 (7)	−0.0779 (7)	0.2992 (5)	2.6 (1)
C16	−0.0304 (9)	−0.4342 (7)	0.1838 (7)	4.3 (2)
C17	0.0291 (8)	0.0275 (9)	0.3589 (6)	4.0 (2)
N21	0.4827 (5)	0.0454 (5)	0.2296 (4)	2.0 (1)
N22	0.4097 (5)	−0.0915 (5)	0.1830 (4)	2.1 (1)
C23	0.4972 (7)	−0.1589 (7)	0.1907 (5)	2.7 (1)
C24	0.6295 (7)	−0.0632 (7)	0.2443 (5)	3.0 (1)
C25	0.6179 (6)	0.0615 (7)	0.2669 (5)	2.5 (1)
C26	0.4504 (9)	−0.3112 (8)	0.1465 (7)	4.5 (2)
C27	0.7367 (7)	0.1992 (8)	0.3217 (6)	3.6 (2)
N31	0.2565 (6)	0.0968 (5)	0.0931 (4)	2.1 (1)
N32	0.2412 (6)	−0.0398 (5)	0.0644 (4)	2.3 (1)
C33	0.1917 (7)	−0.0667 (7)	−0.0250 (5)	2.8 (2)
C34	0.1757 (8)	0.0545 (8)	−0.0557 (5)	3.2 (2)
C35	0.2149 (7)	0.1527 (7)	0.0184 (5)	2.4 (1)
C36	0.165 (1)	−0.2048 (8)	−0.0779 (6)	4.4 (2)
C37	0.2186 (9)	0.2998 (8)	0.0195 (6)	3.9 (2)
B	0.2479 (8)	−0.1487 (7)	0.1339 (6)	2.4 (2)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

of $HB(Me_2pz)_3^-$), 5.86 (s, 1 H, CH of $HB(Me_2pz)_3^-$), 5.89 (s, 1 H, CH of $HB(Me_2pz)_3^-$). ^{13}C NMR (CH_2Cl_2): δ 12.50, 12.58, 12.61, 12.66, 12.81, 12.98, 15.33, 16.04, 16.54, 16.94, 43.91, 44.39, 44.61, 45.51, 53.02 (CH_2Cl_2), 57.80, 106.46, 106.53, 144.36, 144.47, 145.51, 152.46, 152.95, 155.00, 202.56, 207.04, 227.34, 228.77, 247.02. Electronic spectrum ($CHCl_3$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 630 (1320), 438 (44 700), 325 (sh, 16 500), 285 (27 500).

Crystal Structure Determination. Crystals of **1** were grown by slow diffusion of methanol into a dichloromethane solution of the complex. Crystal data for **1**, together with details of the X-ray diffraction experiment, are reported in Table I. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range $20 < 2\theta < 30°$. Two reflections monitored after every 98 data reflections showed a total 12.4% loss in intensity throughout data collection; an anisotropic decay correction was therefore applied (correction factor range 0.851–1.051, average 0.976). An empircal absorption correction based upon a series of ψ-scans was applied to the data.

The position of the W atom was determined from the Patterson map. The remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were included in the refinement but were constrained to ride on the atoms to which they are bonded. Successful refinement of the structure supported the choice of space group $P\bar{1}$. Scattering factors were taken from Cromer and Waber.[37] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[38] In the final cycles of refinement the non-hydrogen atoms were refined anisotropically. All calculations were performed on a VAX computer using SDP/VAX.[39] The final atomic coordinates for all non-hydrogen atoms may be found in Table II. Selected bond distances and angles are given in Table III.

Table III. Selected Bond Distances (Å) and Angles (deg) in **1**

W–S1	2.542 (1)	W–S2	2.590 (1)
W–C40	2.028 (5)	W–C50	1.904 (5)
W–N11	2.208 (4)	W–N21	2.309 (3)
W–N31	2.210 (4)	S1–C1	1.708 (4)
S2–C1	1.707 (4)	C1–N2	1.324 (6)
C40–O40	1.134 (6)	C50–O50	1.195 (6)

S1–W–S2	66.28 (3)	S1–W–C40	127.8 (1)
S1–W–C50	99.0 (1)	S1–W–N11	78.0 (1)
S1–W–N21	81.0 (1)	S1–W–N31	153.6 (1)
S2–W–C40	68.0 (1)	S2–W–C50	80.9 (1)
S2–W–N11	141.8 (1)	S2–W–N21	103.3 (1)
S2–W–N31	139.8 (1)	C40–W–C50	97.5 (2)
C40–W–N11	150.1 (2)	C40–W–N21	86.1 (20)
C40–W–N31	74.1 (2)	C50–W–N11	92.0 (2)
C50–W–N21	175.3 (1)	C50–W–N31	91.4 (2)
N11–W–N21	83.4 (1)	N11–W–N31	77.4 (1)
N21–W–N31	86.8 (1)	W–S1–C1	92.4 (2)
W–S2–C1	90.8 (1)	S1–C1–S2	110.5 (2)
W–C40–O40	175.8 (5)	W–C50–O50	178.1 (4)

Results

Syntheses for compounds **1** and **2** and analytical and IR, NMR, and electronic spectroscopic data are presented in the Experimental Section. A structural study was undertaken for **1**, whose results are summarized in Tables I–III. These results will be introduced at appropriate places in the sections which follow.

Discussion

The reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ with tetraethylthiuram disulfide in acetonitrile is thermally initiated at about 60 °C. The products of the reaction, which result from oxidative decarbonylation and ligand dissociation and fragmentation processes, are dependent upon reaction conditions, most importantly reaction temperature and time. At temperatures of 70–85 °C and intermediate reaction times, the carbonyl complexes **1** and **2** may be detected and isolated. Complete decarbonylation of $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ takes place under conditions of prolonged (ca. 24 h) reflux in acetonitrile.[34] The formation and disappearance of the various carbonyl products was conveniently followed by solution infrared spectroscopy. When closed reaction mixtures containing a 1:2 ratio of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ and Et_4tds were monitored by solution infrared spectroscopy (for example, see Figure 1), the strong ν(CO) bands of $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ (for Figure 1, 1877 s (20%), 1742 s (10% transmission at $t = 0$) cm^{-1}) were replaced by ν(CO) bands characteristic of the carbonyl products. First to appear (within minutes at 80 °C) were bands at ca. 1950 and 1815 cm^{-1}, indicative of the presence of **1** (**1** can also be detected, as a yellow band which moves with the solvent front, by thin-layer chromatography using silica/dichloromethane). The bands due to **1** continued to increase in intensity at the expense of those of $[\{(HB(Me_2pz)_3\}W(CO)_3]^-$ and later (Figure 1, 1 h) a new band appears as a shoulder at 1886 cm^{-1}. Eventually (Figure 1, 3 h) all of the $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ was consumed and bands at 1815 sh, 1825, 1886, and ca. 1950 cm^{-1} dominated the spectrum. The intensities of the carbonyl peaks decreased dramatically up to this stage of the reaction suggesting that decarbonylated species[34] were formed even at these early stages of the reaction. As the reaction proceeded (Figure 1, 6 h), the band at 1886 cm^{-1} decreased considerably and for several hours the nature and concentration of carbonyl species maintained a status quo. Much later in the reactions (Figure 1, 9–24 h) an increase in the intensity of bands at 1815 and 1886 cm^{-1} was evident. These bands signified the presence of **2**, which increased its concentration as the concentration of **1** approached zero (the slight shoulder at 1825 cm^{-1} is due to acetonitrile). We were able to isolate and independently characterize complexes **1** and **2**, but the monocarbonyl species exhibiting the single ν(CO) band at 1886 cm^- has not been isolated. If a mixture of this monocarbonyl species and **1** (reaction time = 3 h) is left to stand at room temperature overnight, the mo-

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(37) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(38) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(39) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

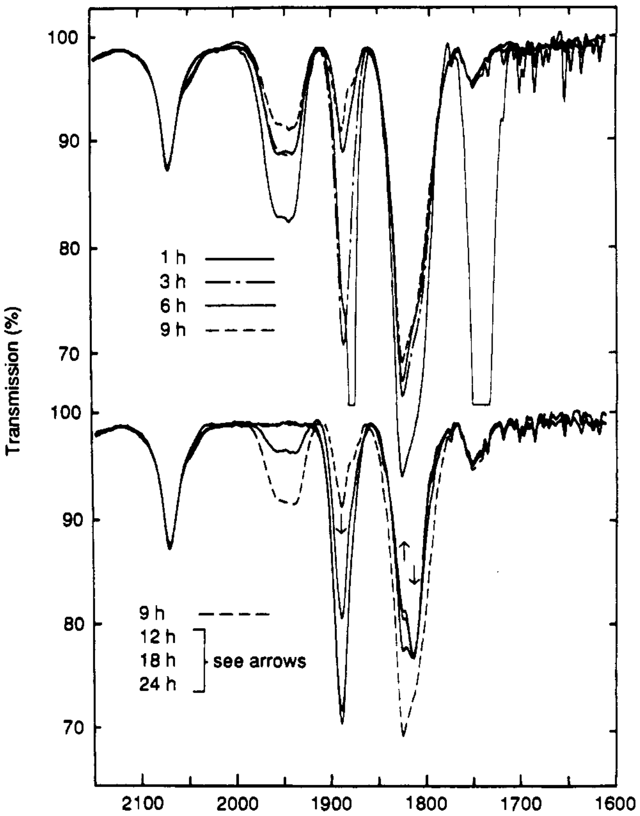

Figure 1. Solution infrared spectra of samples drawn, at the indicated times, from the closed reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ (initial concentration = 2.4 × 10^{-2} M) with Et_4tds (initial concentration = 4.8 × 10^{-2} M) in acetonitrile at 80 °C. Roughly equal intensity bands at 2069 and 1826 cm^{-1} are due to acetonitrile.

nocarbonyl disappears without conversion to **1** or any other carbonyl species. We think it most likely that this species is $\{HB(Me_2pz)_3\}W(CO)(S_2CNEt_2)$. If the above reactions were performed under a slow flow of nitrogen gas, the same products were observed to form in roughly the same sequence but complete decarbonylation was effected within 10 h. Photolysis of the reaction mixture with an intense UV source resulted in the decarbonylation of $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ without the detectable formation of carbonyl species.

Infrared studies revealed that the reactions of $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ with tetramethylthiuram disulfide took a similar course. In the first hours of these reactions, intense bands at 1936 and 1819 cm^{-1}, indicative of the formation of $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNMe_2)$ (**3**), formed as the intensity of the bands due to $[\{HB(Me_2pz)_3\}W(CO_3)]^-$ decreased. At this stage of the reaction attempted isolation of **3** by the method used for **1** (and others) failed. Between 4 and 11 h, a band at 1890 cm^{-1} appeared and then disappeared and bands at 1890 and 1823 cm^{-1}, assigned to $\{HB(Me_2pz)_3\}W(CO)_2(\mu\text{-}S)W(S_2CNMe_2)_2(SCNMe_2)$ (**4**), grew at the expense of bands due to **3**. After 24 h at 80 °C, filtration of the hot reaction mixture permits the isolation in 35% yield of slightly impure green-black **4**. The reactions take a similar course when less than 2 equiv of R_4tds is used, but unreacted $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ may be detected throughout the course of these reactions. Lower temperatures result in slower formation of the carbonyl complexes and make difficult the conversion of **1** into **2**, while higher temperatures increase the rate of formation of the completely decarbonylated products of the reaction.[34] Synthetic procedures developed in response to the above solution IR studies permitted the isolation and characterization of **1** and **2**. We shall now discuss the synthesis, spectroscopy, and structures of these complexes.

Complex 1. This is the first detectable and stable carbonyl product of the title reaction and workup of the reaction mixture immediately following the disappearance of $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ provides the greatest yield of **1**. The relatively low yields of ca. 40–50% are consistent with considerable complete decarbonylation even at the early stages of the reaction. Complex **1** is an air-stable, green-black crystalline solid; the crushed solid and dilute solutions of the complex exhibit a yellow coloration. It is very soluble in chlorinated solvents but insoluble in alcohols and saturated and aromatic hydrocarbons. The complex exhibits two strong, broad ν(CO) bands at ca. 1945 and 1815 cm^{-1} in dichloromethane solution (Figure 2) and solid-state (KBr) infrared spectra, consistent with the presence of a cis arrangement of the carbonyl ligands. The ν(CO) band profiles indicate the presence of several configurations on the IR time scale. The solid-state spectra exhibit bands characteristic of the $HB(Me_2pz)_3^-$ and $S_2CNEt_2^-$ ligands (e.g. ν(BH) 2550, ν(CN) of $S_2CNEt_2^-$ 1495 cm^{-1}). ^1H and $^{13}C\{^1H\}$ NMR spectra reveal that **1** is fluxional on the NMR time scale. In the ^1H NMR spectrum, three singlet resonances, with a 3:9:9 proton integration ratio, may be assigned to the $HB(Me_2pz)_3^-$ ligand and a triplet and a quartet resonance may be assigned to the ethyl substituents of the dithiocarbamate ligand. The dynamic processes which lead to the equivalence of all the pyrazole rings are unclear.

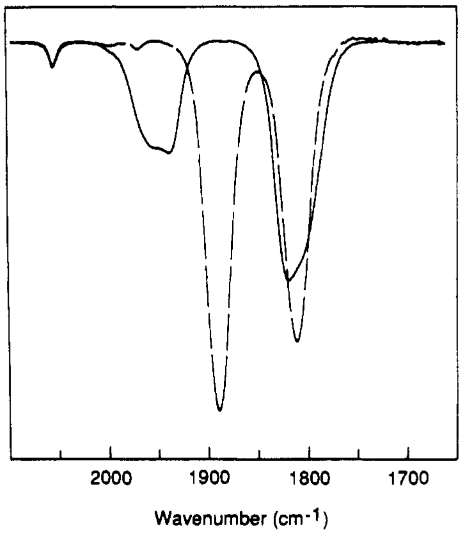

Figure 2. Solution infrared spectra of 10^{-3} M solutions of pure **1** (—) and **2** (- - -) in dichloromethane (solvent peak at 2055 cm^{-1}).

We have examined other synthetic routes to $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ without success; perhaps the most obvious routes are those shown in eqs 4 and 5. Interestingly, dithiocarbamates

$$\{HB(Me_2pz)_3\}W(CO)_3X + S_2CNEt_2^- \rightarrow \mathbf{1} + X^- + CO \qquad (4)$$

$$2\{HB(Me_2pz)_3\}W(CO)_3 + Et_4tds \rightarrow 2\,\mathbf{1} + 2CO \qquad (5)$$

act as reducing agents when reacted with $\{HB(Me_2pz)_3\}W(CO)_3I$[40] and $\{HB(Me_2pz)_3\}W(CO)_3$.[41] Anaerobic reactions involving $\{HB(Me_2pz)_3\}W(CO)_3I$ produce $\{HB(Me_2pz)_3\}W(CO)_3$ or $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ when 1 mol equiv or an excess, respectively, of dithiocarbamate is used. Aerobic reaction of $\{HB(Me_2pz)_3\}W(CO)_3I$ with 1 equiv of NaS_2CNEt_2 results in the formation of an orange compound with an infrared spectrum identical to that of $\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)WO(CO)\{HB(Me_2pz)_3\}$.[42] Both $\{HB(Me_2pz)_3\}W(CO)_3I$ and $\{HB(Me_2pz)_3\}W(CO)_3Br$ are known to be oxidized by molecular oxygen to form the carbonyloxotungsten(IV) complexes $\{HB(Me_2pz)_3\}WO(CO)X$ (X = I^-, Br^-).[40]

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(40) Feng, S. G.; Luan, L.; White, P.; Brookhart, M.; Templeton, J. L.; Young, C. G. *Inorg. Chem.* **1991**, *30*, 2582–2584.

(41) The compound was prepared by ferrocenium oxidation of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ (Templeton, J. L.; Philipp, C. C. Unpublished results). The Mo analogue has been reported: Shiu, K.-B.; Lee, L.-Y. *J. Organomet. Chem.* **1988**, *348*, 357–360.

(42) Young, C. G.; Gable, R. W.; Mackay, M. F. *Inorg. Chem.* **1990**, *29*, 1777–1779.

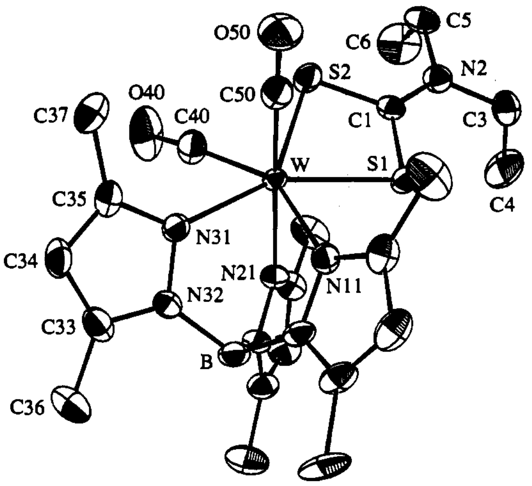

Figure 3. ORTEP view of **1**, showing the atom-labeling scheme. The numbering of the atoms in the pyrazole rings containing N11 and N21 parallels that shown for the ring containing N31. Hydrogen atoms have been omitted for clarity, and ellipsoids have been drawn at the 50% probability level.

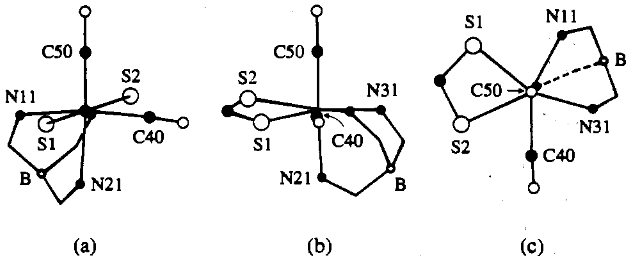

Figure 4. Views of the ligand sphere of **1**: (a) along the C1⋯W vector; (b) along the C40⋯W vector; (c) along the C50⋯W vector (in this view the dashed pyrazole fragment is not bonded in the equatorial girdle). For clarity, partial HB(Me$_2$pz)$_3$$^-$ and S$_2$CNEt$_2$$^-$ ligand fragments are used and not all N(n1) atoms are labeled. In all structures the unlabeled central atom is W.

Structure of 1. An ORTEP diagram of a molecule of **1** is given in Figure 3 along with the atom-labeling scheme employed in the structure determination. Views of the coordination sphere of the complex are given in Figure 4. The coordination geometry of the complex is best described as pentagonal bipyramidal, albeit severely distorted. The pentagonal bipyramid is defined by axial donor atoms C50 and N21 and equatorial donor atoms C40, S1, S2, N11, and N31. The equatorial girdle is composed of a carbonyl ligand, a bidentate dithiocarbamate ligand, and two nitrogen donor atoms of the HB(Me$_2$pz)$_3$$^-$ ligand. The HB(Me$_2$pz)$_3$$^-$ ligand spans the equatorial girdle and one axial site, while the second carbonyl ligand is coordinated to the remaining axial site. As shown in Figure 4a,b, there is considerable puckering of the atoms in the equatorial girdle. Atoms W, S1, S2, N11, N31, and C40 lie 0.0696 (2), −0.297 (2), 0.345 (2), 0.137 (6), 0.052 (6) and −0.307 (8) Å from the best plane defined by these atoms (negative displacements are toward N21). A major distortion in the equatorial girdle results from the tilting of the plane of the dithiocarbamate ligand with respect to the plane containing tungsten and the remaining equatorial donor atoms. This distortion is characterized by a dihedral angle ca. 20° between the planes defined by W, S1, S2, and C1 on one hand and W, N11, N31, and C40 on the other. This distortion relieves steric interactions between S1 and S2 and the methyl groups containing C17 and C27, respectively. Interaction of S1 and C17 and congestion within the equatorial girdle close down the N11–W–N31 angle (77.4 (1)°) relative to the N11–W–N21 and N21–W–N31 angles (83.4 (1) and 86.8 (1)°, respectively). The close pentagonal coordination geometry of the equatorial donor atoms is illustrated in Figure 4c, a view down the pseudoaxis defined by C50, W, and N21. The geometrical constraints of the facially coordinated HB(Me$_2$pz)$_3$$^-$ ligand also contribute to the distortion of the coordination sphere.

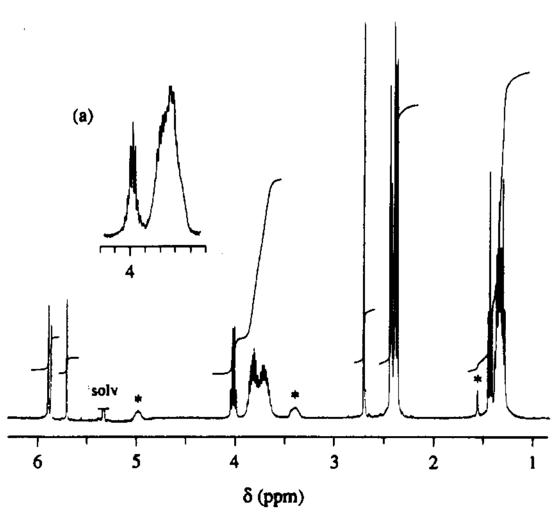

Figure 5. ^{1}H NMR spectra of **2** in CD$_2$Cl$_2$ at 25 °C. Insert a shows the δ 3.5–4.2 region of the CDCl$_3$ spectrum. Asterisked peaks indicate paramagnetic decomposition products or solvent impurity.

The dithiocarbamate ligand in **1** is bonded in a symmetrical bidentate fashion to the W center; W–S1 and W–S2 distances of 2.542 (1) and 2.590 (1) Å, respectively, are observed. The longer of the two bonds is associated with S2, which is cis to both carbonyl ligands. The S1–W–S2 angle of 66.28 (3)° is slightly compressed relative to those of related equatorial ligands in other pentagonal bipyramidal complexes of tungsten; for example, the S–W–S angles of the equatorial ligands in [WS(S$_2$CNEt$_2$)$_3$]$^+$ average 68.65°.[43] The sterically unencumbered axial carbonyl ligand is nearly linear (W–C50–O50 = 178.1 (4)°) and possesses a W–C distance (W–C50 = 1.904 (5) Å) which is significantly shorter than the W–C bond of the equatorial carbonyl ligand (W–C40 = 2.028 (5) Å, W–C40–O40 = 175.8 (5)°). The bond distances and angles within the HB(Me$_2$pz)$_3$$^-$ and S$_2$CNEt$_2$$^-$ ligands are consistent with those of other complexes possessing these ligands.[33,44] The C–N (1.324 (6) Å) and C–S (average 1.707 (4) Å) bond distances of the dithiocarbamate ligand are intermediate between respective single- and double-bond distances (C–N = 1.47, C=N = 1.27, C–S = 1.81, C=S = 1.61 Å[45]) indicative of delocalized π-bonding in the S$_2$CN portion of the ligand. As expected for a ligand with such thioureide character, the six atoms defining the rigid S$_2$CNC$_2$ skeleton are coplanar (maximum displacement = 0.02 Å for C3). The dihedral angle between the S$_2$C and NC$_2$ planes of this ligand is 1.7°. A number of seven-coordinate tungsten tris(pyrazolyl)borate complexes have been structurally characterized,[46] but we are not aware of any such complexes containing the HB(Me$_2$pz)$_3$$^-$ ligand. Of course, seven-coordination is a dominant feature of W(II) chemistry in general.[6]

Complex 2. This was characterized on the basis of analytical, spectroscopic, and preliminary X-ray diffraction data. Elemental analyses and integrated ^{1}H NMR spectra were consistent with the empirical formulation "{HB(Me$_2$pz)$_3$}W$_2$(CO)$_2$(S$_2$CNEt$_2$)$_3$", leaving aside any solvent of crystallization revealed by both techniques. In a dinuclear complex of this formulation, one tungsten center must be coordinated by the HB(Me$_2$pz)$_3$$^-$ ligand and a number of the remaining ligands, or fragments thereof (we

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(43) Snow, M. R.; Tiekink, E. R. T.; Young, C. G. *Inorg. Chim. Acta* **1988**, *150*, 161–162.

(44) Young, C. G.; Roberts, S. A.; Ortega, R.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938–2946.

(45) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(46) For example see: (a) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1984**, *3*, 1124–1126. (b) Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1623–1625. (c) Green, M.; Howard, J. A. K.; James, A. P.; Jelfs, A. N. M.; Nunn, C. M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 1697–1708. (d) Hoskins, S. V.; James, A. P.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1986**, 1709–1716.

Table IV. Spectroscopic Properties of Known Molybdenum and Tungsten Thiocarboxamido Complexes

complex	ν(CN) of $SCNR_2$, cm^{-1}	$\delta(S^{13}CNR_2)$ (J_{W-C}, Hz)	ref
$CpMo(CO)_2(SCNMe_2)$	1573 s		7, 8
$Mo_2S_2(SCNPr^n{}_2)_2(S_2CNPr^n{}_2)_2$			9
$Mo_2S(HC_2Ph)(S_2CNMe_2)_3(SCNMe_2)$	1550 w		10
$Mo_2S(HC_2Bu)(S_2CNMe_2)_3(SCNMe_2)$	1548 m	262.19	10
$Mo_2S(EtC_2Et)(S_2CNMe_2)_3(SCNMe_2)$	1545 m	263.72	10
$Mo_2S(HC_2Ph)(S_2CNEt_2)_3(SCNEt_2)$	1525 m	259.77	10
$Mo_2S(MeC_2Ph)(S_2CNMe_2)_3(SCNMe_2)$	1550 w	262.43	10
$W(S_2CNEt_2)(SCNEt_2)(CO)(CHSPh)$	1526 s	256.9 (111)	11
$W(S_2CNEt_2)(SCNEt_2)(CO)(CHSMe)$	1525 s	256.6 (108)	11
$WS(PhC_2Ph)(S_2CNMe_2)(SCNMe_2)$	1558		12
$WS(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$	1560	257.5	12, 13
$WCo_2(HC_2H)S(CO)_5(SCNMe_2)(S_2CNMe_2)$		249.2	14
$WCo_2(HC_2H)S(CO)_5(SCNEt_2)(S_2CNEt_2)$		247.2 (79)	14
$WCo_2(PhC_2Ph)S(CO)_5(SCNEt_2)(S_2CNEt_2)$		244.7 (81)	14
$WCo_2(HC_2Ph)S(CO)_5(SCNEt_2)(S_2CNEt_2)$		245.9	14
$WCo_2S(CO)_4(\mu\text{-}SCNEt_2)(S_2CNEt_2)(PhC_2Ph)$		227.5	14
$WCo_2S(CO)_4(\mu\text{-}SCNEt_2)(S_2CNEt_2)(HC_2Ph)$		229.5	14
$WCo_2S(CO)_4(\mu\text{-}SCNMe_2)(S_2CNMe_2)(MeC_2Me)$		231.5	14
$WCo_2S(CO)_4(\mu\text{-}SCNMe_2)(S_2CNMe_2)(PPh_3)(HC_2H)$		249.5	14

do not believe $HB(Me_2pz)_3^-$ acts as a bridging ligand here). The presence of two strong ν(CO) bands at 1886 and 1815 cm^{-1} in the infrared spectra of **2** (Figure 2) is consistent with terminal *cis*-dicarbonyl ligands, and in view of the synthesis of **2** from **1**, we assign the two carbonyl ligands to the tungsten atom coordinated by the $HB(Me_2pz)_3^-$ ligand. The second tungsten atom must be bridged to this $\{HB(Me_2pz)_3\}W(CO)_2$ fragment via a dithiocarbamate ligand, or a ligand derived therefrom, and must be complexed solely by such ligands. The complex, solvent-dependent ^1H NMR spectra of **2** are shown in Figure 5. Although the spectra observed in $CDCl_3$ and CD_2Cl_2 are essentially similar, a broad resonance integrating for three $HB(Me_2pz)_3^-$ methyl groups is evidence for partial fluxionality in $CDCl_3$ at room temperature. The inequivalence of all protonic groups within the $HB(Me_2pz)_3^-$ ligand indicates that molecules of **2** are chiral with C_1 symmetry. Moreover, the complexity of the methylene resonances of the various ethyl groups is consistent with the presence of inequivalent diastereotopic H_{AB} methylene groups; a deshielded 9-line CH_2 resonance in the $CDCl_3$ spectrum, assigned to an ABX_3 spin system, appears as a quartet in the CD_2Cl_2 spectrum. The $^{13}C\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 is also consistent with a chiral molecule. Resonances expected for inequivalent pyrazolyl, methyl, and methylene carbons are observed, but most importantly the spectrum exhibits two $S_2\mathit{C}NEt_2^-$ resonances (δ 202.56 and 207.04), two *C*O resonances (δ 227.34 and 228.27), and a peak at δ 247.02 which is assigned to the $S\mathit{C}NEt_2^-$ resonance of a thiocarboxamido ligand. The chemical shifts observed for other thiocarboxamido complexes of molybdenum and tungsten are given in Table IV; the thiocarboxamide carbon resonance of **2** is slightly deshielded relative to those of other mononuclear W(IV) complexes but similar to values observed in many thio-bridged WCo_2 complexes. The NMR spectra of **2** support the predominance in solution of only one chiral species. Only one band is observed in the ν(C═N) region of the infrared spectrum of **2**, and thus, it is not possible using this technique to detect the presence of the thiocarboxamide ligand (see Table IV; most compounds containing dithiocarbamate ligands show a second ν(CN) band assignable to that ligand). Preliminary crystallographic studies[47] of **2** support the presence of a W–S–W bridge leading to the conclusion that **2** is composed of sulfur-bridged $\{HB(Me_2pz)_3\}W^{II}(CO)_2(\mu\text{-}S)$ and $(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(SCNEt_2)$ moieties. The six-coordinate W(II) moiety is presumed to possess a mirror plane of symmetry, but although the W(IV) moiety is likely to possess a pentagonal bipyramidal (PBP) structure, its symmetry and the ligand arrangement at tungsten is uncertain. The chirality of **2** must result from asymmetry at the W(IV) center or to overall molecular asymmetry. If the thiocarboxamide ligand chelates in the equatorial plane of a PBP center, two diastereomeric forms of the complex would be expected depending on the orientation of the ligand. The chirality of $MoO(S_2)(S_2CNR_2)_2$ complexes has a similar origin, and recent ^1H NMR studies of these complexes reveal spectral features related to those of **2**.[48] If the thiocarboxamide ligand spans axial and equatorial PBP sites, then the $(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(SCNEt_2)$ moiety also possesses a mirror plane of symmetry; in this case non-coincidence of the local mirror planes containing W(II) and W(IV) would produce a number of diastereomers depending upon the angle between the planes and the orientation of the thiocarboxamide ligand. In either case, the presence of only one chiral diastereomer is indicated by the NMR spectra. We note that there is precedence and an electronic preference for the last mentioned mode of thiocarboxamide binding.[10,12,13] In the electron-impact mass spectra of **2**, the only tungsten containing ions with *m/z* greater than 550 were observed at 569 and 597, corresponding to the $[\{HB(Me_2pz)_3\}W(CO)_2S]^+$ and $[W(S_2CNEt_2)_2(SCNEt_2)]^+$ fragments predicted for cleavage at the $S\text{–}W^{IV}$ bond; these ions were of very low intensity (0.75%). A striking feature of the electronic spectrum of **2** is the presence of two very intense bands in the visible region at 630 nm (ϵ 1320) and 438 nm (ϵ 44 700).

Mixed-valence compounds are attracting increased attention due to their importance in chemistry, physics, geology, and biology,[49] and a timely and exhaustive review of early transition metal compounds of this type has appeared.[50] About 15 dinuclear mixed-valence tungsten complexes have been reported to date. None of these contain dithiocarbamate or poly(pyrazolyl)borate ligands, but there are examples of complexes containing the metal in oxidation states of +2 and +4. These include the complexes $W_2(NMe_2)_{4-x}(O^iPr)_xCl_2(py)_2(CO)$ (x = 0, 1, 2),[51] which are proposed to possess an unsymmetrical confacial bioctahedral structure in which the CO ligand is bonded to the soft W(II) center, and $W_2H_5(\mu\text{-}PMe_2)(PMe_3)_5$.[52] With its unusual com-

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(47) A number of crystals from several batches of **2** were examined, and data were collected from three of these crystals. The best results were obtained from $2{\cdot}CH_2Cl_2$, which formed monoclinic crystals, space group $P2_1$ with a = 10.360 Å, b = 17.272 (3) Å, c = 13.477 (2) Å, β = 98.68 (1)°, V = 2383.9 Å^3, and Z = 2. A partial structure was determined using 2897 unique reflections with $I > 3.0\sigma(I)$. The coordinates of the tungsten atoms were determined from a Patterson map. Subsequent Fourier syntheses revealed a nearly linear W–S–W fragment and showed that all remaining sulfur atoms were bound to the same tungsten atom. However, the apparent disorder in the $W(S_2CNEt_2)_2(SCNEt_2)$ fragment could not be resolved, and the geometrical parameters for the pyrazolylborate ligand were unsatisfactory.

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position and structure, complex **2** is unique among mixed-valence complexes of the early transition metals.

The mechanism of formation of **2** is uncertain but probably involves the reaction of **1** with one of a number of completely decarbonylated products devoid of the $HB(Me_2pz)_3^-$ ligand. The bridging thio ligand and the thiocarboxamide ligand are likely to be formed from a single dithiocarbamate ligand upon dinucleation and formation of **2**. The prolonged reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ with Et_4tds results in complete oxidative decarbonylation, and a number of products have been identified; these include $\{HB(Me_2pz)_3\}WS(S_2CNEt_2)$, $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$, and $[W(S_2CNEt_2)_4]^+$.[34]

By all accounts, somewhat simpler chemistry pertains to the related cyclopentadienyl (Cp) systems. The analogues of **1**, $CpW(CO)_2(S_2CNR_2)$ (R = Me, Et, piperidinyl), have been known for many years and were originally synthesized by thermally initiated metathical reactions involving $CpW(CO)_2X$ and dithiocarbamate salts.[53,54] Interestingly, the molybdenum complex $CpMo(CO)_2(S_2CNEt_2)$ is formed upon oxidative decarbonylation of $[CpMo(CO)_3]_2$ by Et_4tds in refluxing methylcyclohexane.[55] Abrahamson and co-workers[56] have reported that the photochemically induced oxidation of $[CpW(CO)_3]_2$ by Me_4tds initially results in the quantitative formation of $CpW(CO)_3(\eta^1\text{-}S_2CNMe_2)$. Subsequent loss of a carbonyl ligand and chelation of the dithiocarbamate ligand to form $CpW(CO)_2(S_2CNMe_2)$ may be thermally or photochemically induced. It is interesting to note that oxidation of $CpW(CO)_3(S_2CNMe_2)$ with I_2 produces two major products, one of which is formulated as $CpW(CO)I_2(SCNMe_2)$.[56b]

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Supplementary Material Available: Tables of full crystallographic data, bond distances and angles, and anisotropic thermal parameters (4 pages); a table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Products of Complete Oxidative Decarbonylation of Tricarbonyl{hydrotris(3,5-dimethyl-1-pyrazolyl)borato}tungstate(0) by Tetraalkylthiuram Disulfides: $\{HB(Me_2C_3N_2H)_3\}WS(S_2CNEt_2)$, $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$, and $[W(S_2CNEt_2)_4]^+$

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The final products of the reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ and tetraethylthiuram disulfide in refluxing acetonitrile include the red, diamagnetic, air-stable thiotungsten(IV) complex $\{HB(Me_2pz)_3\}WS(S_2CNEt_2)$ (**1**) and known $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$ (**2**) and $[W(S_2CNEt_2)_4]^+$ (isolated as chloride salt **3**). The intermediate products of this reaction, $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ and $\{HB(Me_2pz)_3\}W(CO)_2(\mu\text{-}S)W(S_2CNEt_2)_2(SCNEt_2)$, are described in the preceding paper in this issue. **1** ($C_{20}H_{32}BN_7S_3W$) crystallizes in triclinic space group $P\bar{1}$ with a = 10.271 (2) Å, b = 10.467 (3) Å, c = 14.222 (4) Å, α = 96.53 (2)°, β = 91.03 (2)°, γ = 118.89 (2)°, V = 1325.4 Å^3, and Z = 2. The structure was solved by Patterson and Fourier methods followed by least-squares refinement, using 3619 reflections, to a conventional R value of 0.045 (R_w = 0.055). The monomeric complex exhibits a distorted octahedral *fac*-N_3–*fac*-S_3 coordination sphere composed of tridentate $HB(Me_2pz)_3^-$, bidentate $S_2CNEt_2^-$ and terminal thio (W═S = 2.153 (2) Å) ligands. The spectroscopic (IR, electronic, ^{1}H NMR, ESR) properties of **1**–**3** are reported.

Introduction

We have recently reported the synthesis and characterization of a number of (dithiocarbamato)molybdenum complexes of the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand, $HB(Me_2pz)_3^-$.[2-5] The complexes $\{HB(Me_2pz)_3\}MoS(S_2CNR_2)$[2] and $\{HB(Me_2pz)_3\}Mo(\eta^1\text{-}S_2CNR_2)(\eta^2\text{-}S_2CNR_2)$[3,4] (R = Me, Et) are of most relevance to the chemistry described herein. The thiomolybdenum(IV) complexes $\{HB(Me_2pz)_3\}MoS(S_2CNR_2)$ were formed by reacting the oxomolybdenum(IV) analogues with boron sulfide and are rare examples[6] of mononuclear thiomolybdenum complexes. The oxomolybdenum(IV) precursors were prepared

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