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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(53) Abel, E. W.; Dunster, M. O. *J. Chem. Soc., Dalton Trans.* **1973**, 98-102.

(54) Glass, W. K.; Shiels, A. *J. Organomet. Chem.* **1974**, *67*, 401-405.

(55) Cotton, F. A.; McCleverty, J. A. *Inorg. Chem.* **1964**, *3*, 1398-1402.

(56) (a) Abrahamson, H. B.; Freeman, M. L. *Organometallics* **1983**, *2*, 679-681. (b) Abrahamson, H. B.; Freeman, M. L.; Hossain, M. B.; Van Der Helm, D. *Inorg. Chem.* **1984**, *23*, 2286-2293.

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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, $\alpha = 96.53$ (2)°, $\beta = 91.03$ (2)°, $\gamma = 118.89$ (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, ^1H 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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(2) Young, C. G.; Roberts, S. A.; Ortega, R.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938-2946.

(3) Young, C. G.; Roberts, S. A.; Enemark, J. H. *Inorg. Chim. Acta* **1986**, *114*, L7-L8.

(4) Young, C. G.; Roberts, S. A.; Enemark, J. H. *Inorg. Chem.* **1986**, *25*, 3667-3671.

(5) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Yamanouchi, K.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 2647-2652.

(6) Other examples include: $(NEt_4)_2[MoS(S_4)_2]$, (a) Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218-1219. (b) Draganjac, M.; Simhon, E. D.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321-3322. $(PPh_4)_2[MoS(CS_4)_2]$, (c) Coucouvanis, D.; Draganjac, M. *J. Am. Chem. Soc.* **1982**, *104*, 6820-6822. (d) Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349-356.

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by reacting K{HB($Me_2pz)_3$} with $MoO(S_2CNR_2)_2$, which in turn were produced by reacting $MoO_2(S_2CNR_2)_2$ with PPh_3. Difficulties involving the chemistry of $WO_2(S_2CNR_2)_2$ and $WO(S_2CNR_2)_2$[7-9] may be expected to complicate the synthesis of {HB($Me_2pz)_3$}$WE(S_2CNR_2)$ (E = O, S) by a similar route. The novel Mo(III) complexes {HB($Me_2pz)_3$}Mo(η^1-S_2CNR_2)(η^2-S_2CNR_2) were prepared by the oxidative decarbonylation of [{HB($Me_2pz)_3$}$Mo(CO)_3]^-$ by tetraalkylthiuram disulfide ($[S_2CNR_2]_2$ = R_4tds); the ethyl derivative remains the only structurally characterized monodentate dithiocarbamate complex of molybdenum.[3,4] A similar oxidative decarbonylation reaction involving [{HB($Me_2pz)_3$}$W(CO)_3]^-$ might be expected to produce the W(III) analogue {HB($Me_2pz)_3$}$W(S_2CNR_2)_2$. However, high-valent tungsten appears to be considerably more thiophilic than molybdenum and the abstraction of sulfur from dithiocarbamates[10] and thiolate ligands[11] is a recognized process. The formation of thiotungsten complexes in the reaction of [{HB($Me_2pz)_3$}$W(CO)_3]^-$ and thiuram disulfides could therefore be envisaged.

A frequent feature of analogous Mo and W chemistry is the enhanced stability of the W compounds relative to their Mo analogues. Accordingly, the reaction of [{HB($Me_2pz)_3$}$W(CO)_3]^-$ with thiuram disulfides produces a number of isolable products, some resulting from partial oxidative decarbonylation and others from complete oxidative decarbonylation, which are not observed[3,4] in the molybdenum system. As described in the preceding paper in this issue,[12] partial oxidative decarbonylation leads to the formation of {HB($Me_2pz)_3$}$W(CO)_2(S_2CNEt_2)$ and {HB($Me_2pz)_3$}$W(CO)_2(\mu$-S)$W(S_2CNEt_2)_2(SCNEt_2)$. Herein, we describe the products of the complete oxidative decarbonylation of [{HB($Me_2pz)_3$}$W(CO)_3]^-$ by tetraethylthiuram disulfide (Et_4tds), viz., the new thiotungsten(IV) complex {HB($Me_2pz)_3$}$WS(S_2CNEt_2)$ (**1**), $W_2(\mu$-S$)_2(S_2CNEt_2)_4$ (**2**), and $[W(S_2CNEt_2)_4]^+$ (isolated as chloride salt **3**). The formation of these complexes and the observed intermediacy of quite unusual carbonyl complexes[12] highlight the complexity of this oxidative decarbonylation reaction. In contrast to the Mo system,[3,4] the {HB($Me_2pz)_3$}W(η^1-S_2CNEt_2)(η^2-S_2CNEt_2) complex was not detected or isolated during the study described.

Experimental Section

Materials and Methods. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate and NEt_4[{HB($Me_2pz)_3$}$W(CO)_3$] were prepared by the methods described by Trofimenko,[13,14] and Et_4tds was purchased from Aldrich Chemical Co. The disulfide and NEt_4[{HB($Me_2pz)_3$}$W(CO)_3$] 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. Analytical and spectroscopic methods have been described in the preceding paper in this issue.[12] ESR spectra were recorded on a Varian E-9 spectrometer using 1,1-diphenylpicrylhydrazyl as reference.

Synthesis of Compounds. A mixture of NEt_4[{HB($Me_2pz)_3$}$W(CO)_3$] (1.5 g, 2.16 mmol) and Et_4tds (1.3 g, 4.38 mmol) in acetonitrile (40 mL) was refluxed for 16–24 h. The green crystalline precipitate of **2**[10f] was removed by filtration and washed with acetonitrile/methanol (1:1) (the complex may be recrystallized from dichloromethane/acetonitrile mixtures by slow removal of the dichloromethane in vacuo). The volume of the filtrate was then reduced in vacuo to ca. 6 mL. Precipitated pink-red **1** was isolated by filtration in air and was washed with a small amount of acetonitrile (complex **1** may be recrystallized from dichloromethane by addition of methanol). The filtrate was then treated with methanol (10 mL) and a large volume of diethyl ether, whereupon a brown oil formed. Following decantation, the oil was dissolved in dichloromethane (30 mL) and the solution was washed with water (2 × 80 mL). The dichloromethane fraction was dried over sodium sulfate and then treated with diethyl ether to precipitate khaki-colored crystals of **3**.[15,16]

Table I. Crystallographic Data for **1**

chem formula $C_{20}H_{32}BN_7S_3W$	formula mass 661.38
a = 10.271 (2) Å	space group $P\bar{1}$
b = 10.467 (3) Å	T = 23 (1) °C
c = 14.222 (4) Å	λ = 0.71073 Å
α = 96.53 (2)°	ρ_{obsd} = 1.65 g cm^{-3}, ρ_{calcd} = 1.66 g cm^{-3}
β = 91.03 (2)°	μ = 47.0 cm^{-1}
γ = 118.89 (2)°	$R(F_o)$ = 0.045[a]
V = 1325.4 Å^3	$R_w(F_o)$ = 0.055[a]
Z = 2	

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

Characterization Data. $W_2(\mu$-S$)_2(S_2CNEt_2)_4$ **(2)**.[10f] Yield = 0.18 g, 16%. Anal. Calcd for $C_{20}H_{40}N_4S_{10}W_2$: C, 23.44; H, 3.93; N, 5.47; S, 31.29. Found: C, 23.58; H, 3.95; N, 5.44; S, 31.14. Infrared spectrum (KBr): 2980 m, 2940 m, 2880 m, 1500 s, 1490 sh, 1450 m, 1435 m, 1420 m, 1377 w, 1353 m, 1270 s, 1205 w, 1147 m, 1140 m, 1085 m, 1075 m, 990 w, 910 w, 845 w, 835 w, 810 w, 560 w, 430 m, 370 w, 360 sh, w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.89 (12 H, t, J = 7.5 Hz, 4 × CH_3), 1.44 (12 H, t, J = 7.5 Hz, 4 × CH_3), 3.30 (8 H, q, J = 7.5 Hz, 4 × CH_2), 4.08 (8 H, q, J = 7.5 Hz, 4 × CH_2). Electronic spectrum ($CHCl_3$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 690 (2670), 600 sh (1490), 450 sh (7550), 370 sh (19600), 346 (24300), 270 (47500).

{HB($Me_2pz)_3$}$WS(S_2CNEt_2)$ (1). Yield = 0.42 g, 30%. Anal. Calcd for $C_{20}H_{32}BN_7S_3W$: C, 36.32; H, 4.88; N, 14.83; S, 14.54. Found: C, 36.28; H, 4.85; N, 14.70; S, 14.60. Infrared spectrum: 2980 m, 2930 m, 2540 m, 1544 s, 1512 s, 1447 s, 1415 s, 1365 s, 1280 w, 1260 w, 1205 s, 1146 w, 1060 m, 1035 m, 980 w, 910 w, 854 m, 825 w, 815 w, 785 m, 735 m, 693 m, 645 m, ν(W=S) 490 m, 350 w cm^{-1}. ^{1}H NMR spectrum (CD_2Cl_2, 20 °C): δ 1.45 (t, 6 H, 2 × CH_3 of $S_2CNEt_2^-$), 2.15 (d (br), 6 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 2.75 (s (br), 6 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 3.15 (s (br), 6 H, 2 × CH_3 of $HB(Me_2pz)_3^-$), 4.10 (q, 4 H, 2 × CH_2 of $S_2CNEt_2^-$), 5.50 (s (br), 1 H, CH of $HB(Me_2pz)_3^-$), 6.20 (s (br), 2 H, 2 × CH of $HB(Me_2pz)_3^-$) (see discussion with regard temperature dependence of NMR). Electronic spectrum (CH_2Cl_2, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 800 (100), 720 sh (50), 530 (400), 365 sh (620).

$[W(S_2CNEt_2)_4]$Cl (3).[15,16] Yield = 0.4 g, 23%. Anal. Calcd for $C_{20}H_{40}ClN_4S_8W$: C, 29.56; H, 4.96; N, 6.89; S, 31.57. Found: C, 29.60; H, 5.00; N, 6.89; S, 31.49. Infrared spectrum (KBr): 2980 m, 2940 m, 2880 m, 1525 s, 1460 s, 1440 s, 1380 m, 1360 s, 1285 s, 1210 s, 1155 m, 1075 m, 1000 w, 860 w, 790 w, 740 w, 580 w, 355 m cm^{-1}. Electronic spectrum ($CHCl_3$, λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 706 (170), 593 (220), 518 (sh, 500), 475 (2230), 446 (sh, 2600), 406 (sh, 2600), 396 (11000), 358 (5300). ESR spectrum (CH_2Cl_2, 20 °C): $\langle g\rangle$ = 1.895, $\langle a(^{183}W)\rangle$ = 60 × 10^{-4} cm^{-1}.

Alternative Synthesis of {HB($Me_2pz)_3$}$WS(S_2CNEt_2)$. A mixture of {HB($Me_2pz)_3$}$W(CO)_2(S_2CNEt_2)$[12] (0.22 g, 0.32 mmol) and cyclohexene sulfide (0.04 mL, 0.35 mmol) in acetonitrile (10 mL) was heated at 85 °C for 4 h with the application of an occassional vacuum to remove evolved carbon monoxide. Upon cooling, the red solid which had precipitated was collected by filtration and was washed with methanol/acetonitrile (1:1). The yield of air dried product was 0.1 g, 47%. Prolonged cooling of the reaction mixture leads to contamination of the product due to the crystallization of {HB($Me_2pz)_3$}$W(CO)_2(\mu$-S)$W(S_2CNEt_2)_2(SCNEt_2)$.[12]

Anal. Calcd for $C_{20}H_{32}BN_7S_3W$: C, 36.32; H, 4.88; N, 14.83; S, 14.54. Found: C, 36.30; H, 4.85; N, 14.86; S, 14.63. The spectroscopic properties of the compound are identical to those given above for {HB($Me_2pz)_3$}$WS(S_2CNEt_2)$.

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(7) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1976**, *17*, L67.

(8) Yu, S.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 4385–4391.

(9) Lee, S.; Staley, D. L.; Rheingold, A. L.; Cooper, N. J. *Inorg. Chem.* **1990**, *29*, 4391–4396.

(10) (a) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182–2186. (b) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745–750. (c) Heckley, P. R.; Holah, D. G. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 865–869. (d) Heckley, P. R.; Holah, D. G.; Brown, D. *Can. J. Chem.* **1971**, *49*, 1151–1160. (e) Peterson, E. J.; Von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1978**, *17*, 1410–1415. (f) Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946–2950. See also: Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 301–469 and references therein.

(11) Recent and representative examples are given: (a) DuBois, M. R.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. J. *J. Am. Chem. Soc.* **1979**, *101*, 5245–5252. (b) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Nicholson, T.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1339–1345. (c) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358–1359.

(12) Young, C. G.; Bruck, M. A.; Wexler, P. A.; Carducci, M. D.; Enemark, J. H. *Inorg. Chem.*, preceding paper in this issue.

(13) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294.

(14) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588–595.

(15) Nieuwpoort, A.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1975**, *95*, 250–254.

(16) Nieuwpoort, A.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1975**, *95*, 289–294.

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

atom	*x*	*y*	*z*	*B*, Å^2
W	0.20915 (4)	0.33499 (4)	0.21691 (3)	2.673 (7)
S1	0.2501 (3)	0.4766 (3)	0.0863 (2)	3.69 (6)
S2	0.0214 (3)	0.1800 (3)	0.0894 (2)	3.46 (6)
S3	0.0875 (3)	0.4185 (3)	0.3014 (2)	4.47 (6)
N1	0.043 (1)	0.3188 (9)	−0.0657 (6)	4.4 (2)
N11	0.1733 (7)	0.1614 (7)	0.3021 (6)	2.9 (2)
N12	0.2912 (7)	0.1511 (8)	0.3443 (6)	3.2 (2)
N21	0.4238 (8)	0.4739 (7)	0.2994 (6)	3.0 (2)
N22	0.4952 (7)	0.4140 (8)	0.3469 (6)	3.3 (2)
N31	0.3683 (7)	0.2469 (7)	0.1478 (6)	2.9 (2)
N32	0.4574 (8)	0.2230 (8)	0.2105 (6)	3.3 (2)
C1	0.095 (1)	0.326 (1)	0.0231 (8)	3.4 (2)
C2	0.109 (1)	0.448 (1)	−0.1181 (9)	5.3 (3)
C3	0.200 (2)	0.433 (2)	−0.192 (1)	8.2 (5)
C4	−0.078 (1)	0.176 (1)	−0.1183 (9)	5.3 (3)
C5	−0.207 (2)	0.178 (2)	−0.145 (2)	10.9 (7)
C11	0.049 (1)	0.055 (1)	0.3310 (8)	3.5 (2)
C12	0.083 (1)	−0.024 (1)	0.3897 (8)	3.8 (2)
C13	0.2374 (9)	0.0383 (9)	0.3952 (7)	3.3 (2)
C14	−0.104 (1)	0.027 (1)	0.3010 (9)	5.4 (3)
C15	0.333 (1)	−0.009 (1)	0.4479 (8)	5.0 (3)
C21	0.499 (1)	0.622 (1)	0.3288 (8)	3.5 (2)
C22	0.619 (1)	0.655 (1)	0.3931 (7)	3.5 (2)
C23	0.616 (1)	0.525 (1)	0.4038 (7)	3.8 (3)
C24	0.454 (1)	0.724 (1)	0.2943 (9)	4.6 (3)
C25	0.718 (1)	0.494 (1)	0.4612 (9)	5.1 (3)
C31	0.404 (1)	0.217 (1)	0.0604 (8)	3.7 (2)
C32	0.512 (1)	0.176 (1)	0.0675 (9)	4.4 (3)
C33	0.545 (1)	0.182 (1)	0.1632 (9)	4.1 (2)
C34	0.337 (1)	0.224 (1)	−0.0310 (8)	4.9 (3)
C35	0.653 (1)	0.144 (1)	0.209 (1)	5.4 (3)
B	0.450 (1)	0.254 (1)	0.3180 (9)	3.4 (3)

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

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

W–S1	2.424 (2)	W–S2	2.413 (2)
W–S3	2.153 (2)	W–N11	2.186 (7)
W–N21	2.185 (6)	W–N31	2.408 (6)
S1–C1	1.741 (9)	S2–C1	1.739 (9)
C1–N1	1.35 (1)		
S1–W–S2	72.32 (8)	S3–W–N21	95.7 (2)
S1–W–S3	98.99 (9)	S3–W–N31	170.2 (2)
S1–W–N11	163.4 (2)	N11–W–N21	88.0 (2)
S1–W–N21	98.6 (2)	N11–W–N31	78.7 (2)
S1–W–N31	88.1 (2)	N21–W–N31	76.4 (2)
S2–W–S3	100.52 (9)	W–S1–C1	88.5 (3)
S2–W–N11	97.0 (2)	W–S2–C1	88.9 (3)
S2–W–N21	162.5 (2)	S1–C1–S2	110.2 (5)
S2–W–N31	88.1 (1)	S1–C1–N1	125.5 (7)
S3–W–N11	95.5 (2)	S2–C1–N1	124.2 (7)

Crystal Structure Determination. Red-orange crystals of **1** were grown from hot acetonitrile. 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 24 reflections in the range $11 < 2\theta < 21°$. Three reflections monitored after every 97 data reflections showed no change in intensity throughout data collection. Data were corrected for absorption using the differential absorption technique of Walker and Stuart,[17] but no decay correction was necessary.

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. The largest peaks in the final difference electron density map were within 2 Å of the proximal methyl groups of the pyrazolylborate ligand. Scattering factors were taken from Cromer and Waber.[18] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[19] In the final cycles of refinement the non-hydrogen atoms were refined anisotropically. All calculations were performed on a VAX computer using SDP/VAX.[20] 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.

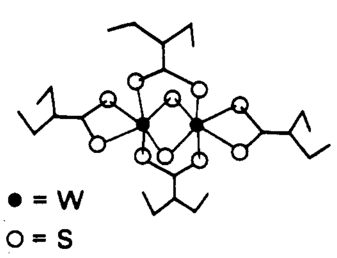

Figure 1. Structure of $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$.

Results

Details of the complete oxidative decarbonylation reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ and Et_4tds, along with analytical and spectroscopic data characterizing the products as **1–3**, 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

Five isolable products result from the reaction of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ with Et_4tds in hot acetonitrile. The products, which result from oxidative decarbonylation and ligand dissociation and fragmentation processes, are dependent upon reaction conditions, especially stoichiometry, temperature, and time. At temperatures of 70–85 °C and intermediate reaction times, the carbonyl complexes $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ and $\{HB(Me_2pz)_3\}W(CO)_2(\mu\text{-}S)W(S_2CNEt_2)(SCNEt_2)$ may be detected and isolated.[12] Complete decarbonylation of $[\{HB(Me_2pz)_3\}W(CO)_3]^-$ takes place under conditions of prolonged (ca. 24 h) reflux in acetonitrile. The three complexes formed under these conditions, **1**, **2**, and $[W(S_2CNEt_2)_4]^+$, may be separated by careful workup of the reaction mixture. The synthesis and spectroscopic characterization of each complex is described in order of isolation—see Experimental Section.

Green **2**, isolated first from the reaction mixture, has been reported by Cotton and co-workers[10f] to form upon reaction of $W(CO)_3(MeCN)_3$ with Et_4tds in acetone at 20 °C. We have been unable to repeat this synthesis. A rapid reaction does take place when Et_4tds is added to a solution of $W(CO)_3(MeCN)_3$ in acetone. The strong solution infrared bands of $W(CO)_3(MeCN)_3$ at 1906 and 1790 cm^{-1} (the latter partially obscured by an intense acetone band at 1715 cm^{-1}) are replaced within 10 min by bands at 2015, 1924, and 1900 cm^{-1}. These bands match closely the $\nu(CO)$ bands of $W(S_2CNEt_2)_2(CO)_3$ in dichloromethane reported by Broomhead and Young.[21] The acetone solution of $W(S_2CNEt_2)_2(CO)_3$ remains unchanged during the execution of the reported[10f] procedure. Reflux of the reaction mixture after the elapse of the 12-h reaction time does result in a green solution, but the species formed is (are) very air-sensitive. There is no indication in the literature, save the fact that the crystallographic study was performed on a crystal coated in epoxy, that **2** is air-sensitive. On the basis of previous studies of the chemistry of $W(S_2CNEt_2)_2(CO)_3$, we suggest that the green species formed upon reflux is $W(S_2CNEt_2)_2(CO)_2(acetone)$. Indeed, samples of **2** prepared by our method are quite stable in air although some decomposition is evident in solution. The complex is only sparingly soluble in chlorinated solvents and virtually insoluble in other solvents. Although it is formed in low yield, the route described herein provides a reproducible synthesis for this interesting complex.

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(17) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

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

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

(20) 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.

(21) Broomhead, J. A.; Young, C. G. *Aust. J. Chem.* **1982**, *35*, 277–285.

As revealed by X-ray crystallography,[10f] the dinuclear complex (Figure 1) is composed of six-coordinate W(IV) centers bridged by two thio and two dithiocarbamate ligands. Each tungsten atom is further coordinated by a bidentate dithiocarbamate ligand. The short W–W distance of 2.530 (2) Å has been ascribed to the presence of a double metal–metal bond. Crystallographic characterization of **2** was not accompanied by any physical or spectroscopic characterization.[10f] Spectroscopic data reported herein are in accordance with expectations and with the maintenance of the solid-state structure in solution. The infrared spectrum of **2** features bands due mainly to dithiocarbamate ligands. In the otherwise uninformative spectrum, several bands appear to be split into two equally intense bands consistent with the presence of two distinct types of dithiocarbamate ligand. These bands occur at ca. 1500 (ν(CN)), 1425, 1140, and 840 cm^{-1} (cf. the single bands present at these wavenumbers in the spectrum of **3**). One other significant feature of the infrared spectrum is a band at 430 cm^{-1}, which occurs in addition to the expected broad band assigned to the ν(W–S) modes of the dithiocarbamate ligands. Bands between 420 and 440 cm^{-1} have been ascribed to the bridging Re–S units in the somewhat related $Re_2(\mu\text{-}S)_2(S_2CNBu^i{}_2)_4$ complex.[22] The ^{1}H NMR spectrum of **2** clearly reveals the presence of two dithiocarbamate ligand environments; an idealized D_{2h} structure results in the equivalence of the ethyl groups of the bridging ligands on the one hand and the nonbridging ligands on the other. Thus, two triplet methyl resonances are observed at δ 0.89 and 1.44 and two quartet methylene resonances are observed at δ 3.30 and δ 4.08. The shielded methyl and methylene resonances are associated with one set of ethyl groups as decoupling of either resonance leads to the collapse of its partner. This situation also applies to the deshielded methyl and methylene resonances.

Red, diamagnetic, air-stable **1** is isolated in 30% yield upon filtration of the reaction mixture (to remove **2**) and evaporation of the filtrate to low volume. The complex is stable in the solid state but slowly decomposes in solution. It is highly soluble in chlorinated solvents, partially soluble in toluene, and insoluble in most other solvents. Recrystallization from dichloromethane/methanol leads to incorporation of solvent in the crystals, but the solvent is lost upon standing in air. To date, very few thiotungsten(IV) complexes have been reported in the literature; these include $WS(PhC_2Ph)(S_2CNEt_2)_2$[10b] and $WS(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$.[10b,23]

In an independent synthesis, complex **1** was produced upon reaction of $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ with cyclohexene sulfide in acetonitrile; precipitation of the product from the reaction mixture assists ready isolation. The simple sulfur atom transfer reaction which results in the formation of **1** is accompanied by side reactions which produce significant amounts of $\{HB(Me_2pz)_3\}W(CO)_2(\mu\text{-}S)W(S_2CNEt_2)(SCNEt_2)$, a product observed at intermediate stages of the title reaction.[12] Episulfides have been employed in related sulfur atom transfer reactions.[10b] In the presence of oxygen atom donors, $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ reacts to form blue $\{HB(Me_2pz)_3\}WO(S_2CNEt_2)$, characterized by infrared bands at 2525 (ν(BH)), 1518 (ν(CN)), and 950 (ν(W=O)) cm^{-1}. Very small amounts of this product are detectable in the title reaction and presumably result from the presence of adventitious oxygen. The synthesis and properties of this complex, whose molybdenum analogue is known,[2] have not been further investigated.

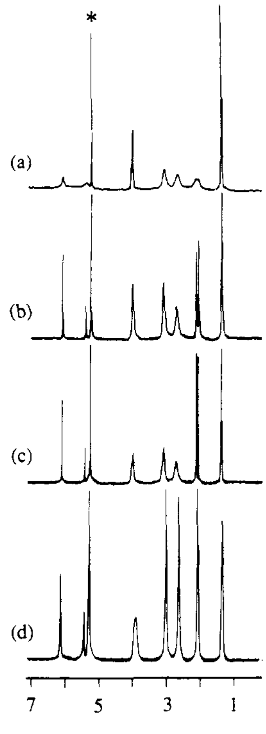

Figure 2. Variable-temperature ^{1}H NMR spectra of **1** in CD_2Cl_2 (δ = 5.32): (a) 20 °C; (b) −30 °C; (c) −60 °C; (d) −100 °C. The solvent peak is identified by an asterisk.

The infrared spectrum of **1** exhibits bands due to $HB(Me_2pz)_3^-$ (ν(BH) = 2540 cm^{-1}), bidentate $S_2CNEt_2^-$ (ν(CN) = 1512 cm^{-1}), and terminal thio (ν(W=S) = 490 cm^{-1}) ligands. The ν(W=S) band is close in energy to those reported for other thiotungsten(IV) complexes, cf. $WS(PhC_2Ph)(S_2CNEt_2)_2$[10b] (485 cm^{-1}) and $WS(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$[10b,23] (490 cm^{-1}), but slightly lower than the corresponding band in $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$ (512 cm^{-1}).[2] In contrast to $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$, which exhibits a ^{1}H NMR spectrum consistent with a stereochemically rigid molecule of C_s symmetry,[2] complex **1** exhibits unusual temperature-dependent ^{1}H NMR spectra (Figure 2). At −100 °C in CD_2Cl_2, the relatively sharp resonances of the $HB(Me_2pz)_3^-$ ligand are consistent with molecular C_s symmetry. Thus, a 2:1 integration of the pyrazole ring protons (δ 5.5–6.5) and a 6:6:(3 + 3) integration of the methyl resonances of the $HB(Me_2pz)_3^-$ ligand are observed. Viscosity broadened resonances at δ 3.9 and 1.4 are observed for the dithiocarbamate ethyl groups. At −60 °C the two deshielded methyl resonances of the $HB(Me_2pz)_3^-$ ligand are considerably broadened while the two shielded methyl resonances remain sharp. The latter are somewhat more separated in chemical shift than in the spectrum at −100 °C. The broadened resonances each integrate for two methyl groups while the two sharp resonances integrate for one methyl group each. The pyrazole ring proton resonances remain sharp, and a triplet is now discernible for the methyl resonance of the dithiocarbamate ligand. With increasing temperature, broadening of all $HB(Me_2pz)_3^-$ ligand resonances continues but at −30 °C the two shielded methyl resonances remain relatively sharp. At 20 °C all the resonances of the $HB(Me_2pz)_3^-$ ligand have become severely broadened while sharp quartet and triplet resonances are produced by the ethyl groups of the dithiocarbamate ligand. At higher temperatures the methyl resonances of the $HB(Me_2pz)_3^-$ ligand continue to broaden and coalesce, but due to the insolubility of **1** in high boiling point solvents, the high-temperature-limiting spectrum could not be obtained. The variable-temperature NMR spectra of **1** are consistent with rotational averaging of the dithiocarbamate ligand ethyl groups as well as, at high temperatures, rotation about the W··B axis of the triangular face capped by the $HB(Me_2pz)_3^-$ ligand. Averaging of the ethyl groups is indicated by the equivalence of the CH_2 protons, which are inequivalent (H_{AB}) in a static molecule of C_s symmetry;[2] at low temperatures this is likely to be effected by a metal-centered rearrangement rather than rotation about the C–N bond. Rotation of triangular faces capped by the related $HBpz_3^-$ ligand have been observed in variable-temperature NMR studies of $[M(HBpz_3)(CO)_2]_2$ (M = Ru, Os).[24]

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(22) Wei, L.; Halbert, T. R.; Murray, H. H.; Steifel, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6431–6433.

(23) Brower, D. C.; Tonker, T. L.; Morrow, J. R.; Rivers, D. S.; Templeton, J. L. *Organometallics* **1986**, *5*, 1093–1097.

(24) Steyn, M. M. de V.; Singleton, E.; Hietkamp, S.; Liles, D. C. *J. Chem. Soc., Dalton Trans.* **1990**, 2991–2997.

The third isolated product of the reaction is **3**. This compound and salts of a wide variety of analogous $[W(S_2CNR_2)_4]^+$ (R = Me, Et, *i*-Pr; $R_2 = (CH_2)_n$, n = 4, 5) complexes have been the subjects of detailed physical,[15] electrochemical,[15] and infrared,[15] electronic,[16] and ESR[16] spectroscopic studies by Nieuwpoort and Steggerda. These extremely stable complexes are formed upon oxidative decarbonylation of $[W(CO)_5X]^-$ complexes by thiuram disulfides.[15] Elemental analysis and infrared, ESR, and electronic spectroscopy unambiguously identify this product. In particular, the unmistakable electronic spectrum of **3** is closely matched by the spectrum of our reaction product. The isolation of the chloride salt of $[W(S_2CNEt_2)_4]^+$ warrants comment. Since there is no source of chloride in the reaction mixture, other anions, most likely diethyldithiocarbamate, must play the role of counterion to $[W(S_2CNEt_2)_4]^+$. Indeed, the compound $[W(S_2CNEt_2)_4](S_2CNEt_2)$ has been isolated, from the reaction of $W(CO)_6$ with excess thiuram disulfide, and characterized by Nieuwpoort and Steggerda.[15] The complex is unstable in chloroform due to a reaction of the anion with the solvent. There are also other reports of the instability of $S_2CNEt_2^-$ and its complexes in halocarbon solvents, and $(R_2NCS_2)_2CH_2$ and $(NH_2Et_2)(S_2CNR_2)$ are known to form upon reaction of NaS_2CNEt_2 with dichloromethane and chloroform, respectively.[25] These observations provide an explanation for the isolation of the chloride salt of $[W(S_2CNEt_2)_4]^+$ from dichloromethane extracts of the actual reaction product, which we propose to be $[W(S_2CNEt_2)_4](S_2CNEt_2)$. Given the excess of thiuram disulfide in our reactions, it is unlikely that $[W(S_2CNEt_2)_4]^+$ results from the air oxidation of $W(S_2CNEt_2)_4$, a known reaction,[15] upon aerial workup.

The mechanisms involved in the formation of the various products remain unclear. Abstraction of sulfur from dithiocarbamate ligands has been reported[10] and in some cases is accompanied by the stabilization of the remaining ligand fragment as a thiocarboxamido ligand.[10a,b] The first example of this type of reaction was reported by Weiss and co-workers,[10a] who synthesized $Mo_2S_2(SCNPr^n{}_2)_2(S_2CNPr^n{}_2)_2$; the complex contains two thiocarboxamide ligands and incorporates the abstracted sulfur into the bis(μ-sulfido) bridge. Recently, Templeton and coworkers[10b] reported the preparation of $WS(PhC_2Ph)(SCNEt_2)(S_2CNEt_2)$, which presumably forms by C–S cleavage of a dithiocarbamate ligand. Indeed, the intermediate formation of the thiocarboxamido complex $\{HB(Me_2pz)_3\}W(CO)_2(\mu\text{-}S)W(S_2CNEt_2)_2(SCNEt_2)$ has been established in the reaction under discussion.[12] There are two possible mechanisms for the formation of **1** which are consistent with the observed intermediates of the reaction. The first involves cleavage of the $S–W^{IV}$ bond of $\{HB(Me_2pz)_3\}W^{II}(CO)_2(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(SCNEt_2)$ to produce $[\{HB(Me_2pz)_3\}WS(CO)_2]^-$, which is then oxidized by thiuram disulfide to yield **1** and $S_2CNEt_2^-$. The second involves C–S bond cleavage in a complex such as $\{HB(Me_2pz)_3\}W(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$, formed by reaction of $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$ with thiuram disulfide. The actual stage of formation of these non-carbonyl products is different to assess, but **1** and $[W(S_2CNEt_2)_4]^+$ appear at intermediate stages of the reaction. The high temperature of the reaction, its evolution of CO, and the formation of paramagnetic species (e.g. $[W(S_2CNEt_2)_4]^+$) have prevented monitoring by NMR spectroscopy. We note that the reaction of dithiocarbamate ligands with acetonitrile is reported to form $R_2NH_2(S_2CNR_2)$ but the other products of the reaction have not been identified.[25] We have not assessed the impact of this possible side reaction on the course of the reaction under discussion.

The behavior of the tungsten system contrasts with that of the recently studied molybdenum system. In the Mo case we showed that the reaction of R_4tds (R = Me, Et) with $NEt_4[\{HB(Me_2pz)_3\}Mo(CO)_3]$ in refluxing acetonitrile resulted in the formation of orange Mo(III) complexes, $\{HB(Me_2pz)_3\}Mo(\eta^2\text{-}S_2CNR_2)(\eta^1\text{-}S_2CNR_2)$.[3,4] When the progress of this reaction was monitored by solution infrared spectroscopy, there was no detectable formation of intermediate carbonyl products such as $\{HB(Me_2pz)_3\}Mo(CO)_2(S_2CNEt_2)$ or $\{HB(Me_2pz)_3\}Mo(CO)_2(\mu\text{-}S)Mo(S_2CNEt_2)_2(SCNEt_2)$; if such products are formed, they must be rapidly oxidized to the observed Mo(III) product. Complexes analogous to **1** were not observed in the reaction involving Mo; however, they may have remained undetected in the mother liquor obtained upon filtration of the major products. In contrast, we have no evidence for the formation of $\{HB(Me_2pz)_3\}W(\eta^1\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)$ in the tungsten system but have noted above this complex's possible intermediacy in the formation of **1**.

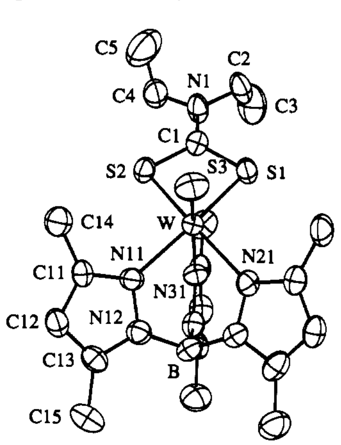

Figure 3. Molecular structure and atom-labeling scheme for **1**. The numbering of the pyrazole rings containing N21 and N31 parallels that shown for the ring containing N11. Thermal ellipsoids are plotted at the 50% probability level, and hydrogen atoms are not included.

Description of the Structure. The unit cell of **1** contains discrete monomeric molecules of $\{HB(Me_2pz)_3\}WS(S_2CNEt_2)$. These six-coordinate molecules exhibit a distorted octahedral coordination geometry and possess approximate C_s symmetry; an ORTEP view of the molecule, along with the atom-labeling scheme, is shown in Figure 3. The structural constraints of the $HB(Me_2pz)_3^-$ ligand restrict it to facial coordination sites, forcing the three sulfur donor atoms to also adopt a facial geometry. The W–S3 bond distance of 2.153 (2) Å is comparable with the W=S distances in other mononuclear thiotungsten(IV) complexes such as $WS(PhC_2Ph)(S_2CNEt_2)_2$[10b] (W=S = 2.147 (2) Å) and $WS(PhC_2Ph)(S_2CNEt_2)(SCNEt_2)$[23] (W=S = 2.138 (5) Å). These seven-coordinate compounds exhibit coordination geometries which may be described as distorted octahedral with the alkyne occupying one coordination site. In the molybdenum analogue $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$ a shorter Mo=S bond distance of 2.129 (2) Å is observed.[2] The W=S bond exerts a strong trans influence, lengthening the W–N31 bond (2.408 (6) Å) by ca. 0.22 Å compared to the nearly equivalent W–N11 and W–N21 bonds. This effect is also observed for $\{HB(Me_2pz)_3\}MoS(S_2CNEt_2)$, where the Mo–N bond trans to Mo=S is ca. 0.26 Å longer than the other Mo–N bonds. The alkyne complexes also exhibit a lengthening of the W–S bond trans to the W=S group compared to the other W–S bonds in these complexes.[10b,23] The W atom is displaced toward S3 by 0.30 (4) Å from the plane defined by S1, S2, N11, and N21. The dithiocarbamate ligand in **1** is bonded in a symmetrical bidentate fashion to the W center; W–S distances of 2.424 (2) Å and 2.413 (2) Å are observed. The bond distances and angles within the $HB(Me_2pz)_3^-$ and $S_2CNEt_2^-$ ligands are consistent with those of other complexes possessing these ligands.[2] The C–N (1.35 (1) Å) and C–S (average 1.740 (9) 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[26]) indicative of delocalized π-bonding in the S_2CN portion of the ligand. As expected for a ligand with such thioureide character, the six atom defining the rigid S_2CNC_2 skeleton are coplanar (maximum displacement =

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(25) Heckley, P. R.; Holah, D. G.; Hughes, A. N.; Leh, F. *Can. J. Chem.* **1970**, *48*, 3827–3830.

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

0.08 (1) Å for C4). The dihedral angle between the S_2C and NC_2 planes of this ligand is 7.8°. The W atom is displaced from the S_2CNC_2 plane toward the S3 atom by 0.183 (4) Å. The structure of **1** is closely related to that of its molybdenum analogue although the bond distances within the coordination sphere of **1** are consistently longer than those of the molybdenum compound.[2]

Acknowledgment. We thank Mr. G. Jamison for the VT-NMR spectra. C.G.Y. completed this work during a sabbatical at the University of North Carolina, Chapel Hill, NC; the hospitality of that institution and the support and encouragement of Prof. J. L. Templeton and his group are gratefully acknowledged. We thank the Australian Research Council for financial support. The structure was determined in the Molecular Structure Laboratory at the University of Arizona.

Supplementary Material Available: Tables of full crystallographic data, bond distances and angles, and anisotropic thermal parameters (5 pages); a table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Rajasthan, Jaipur, India

Studies of Fluorinated 1,3-Diketones and Related Compounds. 17. Benzoic Acid Hydrazide Derivatives of 1,3-Diketones and Their Nickel Complexes. Molecular Structures of $C_6H_5C(=O)\overline{NN=C(p\text{-}FC_6H_4)CH_2C}(OH)(p\text{-}FC_6H_4)$ and $[C_6H_5C(\underline{O)=N\overline{N=C(p\text{-}FC_6H_4)CH=C(O)(p\text{-}FC_6H_4)]}}Ni(NH_3)$

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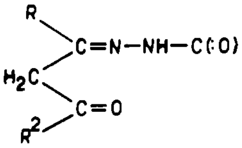
Received March 14, 1990

The synthesis and characterization of some benzoic acid derivatives of 1,3-diketones $R^1C(=O)\overline{NN=C(R)CH_2C}(OH)R^2$ (R^1 = C_6H_5, p-FC_6H_4; R = CH_3, C_2H_5, p-FC_6H_4; R^2 = p-FC_6H_4, 3-CH_3-4-FC_6H_3) and their nickel complexes $[R^2C(\overline{O)=CHC(R)}$-$\overline{=N}\underline{N=C(O)R^1]}Ni(NH_3)$ are reported. Spectral studies reveal that the ligands exist exclusively as cyclic tautomers corresponding to pyrazoline derivatives and undergo a ring-opening reaction on chelation with nickel. The crystal structures of $C_{22}H_{16}F_2N_2O_2$ (I) and its nickel complex $C_{22}H_{17}F_2N_3O_2Ni$ (II) are reported. The crystals of I are orthorhombic, space group *Pbca*, with a = 10.479 (4) Å, b = 16.155 (4) Å, c = 21.451 (4) Å, V = 3631.6 Å^3, Z = 8, M_r = 378.38, D_c = 1.122 g cm^{-3}, μ(Mo Kα) = 0.79 cm^{-1}, $F(000)$ = 1272, and final R = 0.074 for 1887 ($I > \sigma(I)$) of 2643 unique reflections ($2 < \theta < 25°$). The ligand exists in a cyclic tautomeric form with a planar five-membered ring corresponding to a pyrazoline derivative. The crystals of the nickel complex II are triclinic, space group $P\bar{1}$, with a = 7.553 (2) Å, b = 11.154 (3) Å, c = 12.584 (2) Å, α = 77.29 (1)°, β = 87.41 (2)°, γ = 69.93 (2)°, V = 971.1 Å^3, Z = 2, M_r = 452.11, D_c = 1.546 g cm^{-3}, μ(Mo Kα) = 10.43 cm^{-1}, $F(000)$ = 464, and final R = 0.029 for 2643 ($I > \sigma(I)$) of 3436 unique reflections ($2 < \theta < 25°$). In both the cases, λ(Mo Kα) = 0.71069 Å and T = 295 K. The crystal structure shows a square-planar geometry around the nickel atom and the tridentate bifunctional behavior of the ligand.

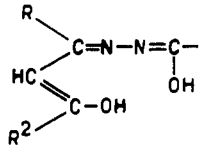
Introduction

1,3-Diketones and related compounds constitute an important class of coordination ligands, and their keto–enol tautomerism has been extensively studied.[1,2] In continuation of our earlier work on the structural studies on ligands derived from 1,3-diketones and their mode of coordination with metals,[3,4] we are now reporting the synthesis and study of some benzoic acid hydrazide derivatives of 1,3-diketones and their nickel complexes.

Benzoic acid hydrazide derivatives of β-dicarbonyl compounds can exist in several distinct isomeric forms, as there are several tautomeric probabilities for these compounds. A survey of the literature[5–9] reveals controversial reports on the solution tautomeric equilibria for such derivatives. Sacconi et al.,[5,6] on the basis of UV spectral studies and the mode of coordination of 1,3-diketone acylhydrazones, proposed that these exist in tautomeric forms corresponding to a hydrazone (A) and its enol form (B), with a predominance of the latter. However, Iskander et al. have reported[7] that the initial product of the condensation of benzoylacetaldehyde and aryoylhydrazines is predominantly the enolimino form rather than the ketoenamine form and the former on cyclization gives a 5-hydroxypyrazoline derivative (C). On the other hand, recent reports[8,9] on the solution tautomeric equilibria of these compounds by NMR investigations suggest that they exhibit ring–chain tautomerism involving an open-chain enehydrazine form (D) and a cyclic 5-hydroxypyrazoline form (C).



(A)



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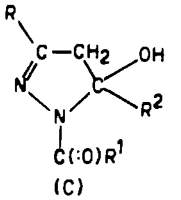

(C)

$R^2C(:O)CH{:}C(R)NHNHC(:O)R^1$

(D)

In view of the these observations, it was considered worthwhile to investigate, in detail, the synthesis and structural aspects of benzoic acid hydrazide derivatives of 1,3-diketones and the rearrangement they may undergo on coordination with nickel. In

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(1) Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic Press: New York, 1978.
(2) Joshi, K. C.; Pathak, V. N. *Coord. Chem. Rev.* **1977**, *22*, 37.
(3) Joshi, K. C.; Joshi, B. S. *J. Fluorine Chem.* **1987**, *36*, 141.
(4) Joshi, K. C.; Joshi, B. S. *Synth. React. Inorg. Met.-Org. Chem.* **1986**, *16*, 1009.
(5) Sacconi, L. *Z. Anorg. Allg. Chem.* **1954**, *275*, 249.
(6) Sacconi, L.; Paoletti, P.; Maggio, F. *J. Am. Chem. Soc.* **1957**, *79*, 4067.
(7) Reteb, L.; Azmy, B.; Nashed, M. A.; Iskander, M. F. *Z. Naturforsch, B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1527.
(8) Yakimovich, S. I.; Nikolaev, V. N.; Kutsenko, E. Yu. *Zh. Org. Khim.* **1982**, *18*, 762.
(9) Vakimovich, S. I.; Nikolaev, V. N. *Zh. Org. Khim.* **1983**, *19*, 880.

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