188 *Inorg. Chem.* **1982**, *21*, 188–192

MeEtCO, 78-93-3; *t*-BuMeCO, 75-97-8; *t*-Bu(*i*-Pr)CO, 5857-36-3; (*R*)-PhMeC(H)OSi(C_6H_5)$_2$H, 55630-27-8; (*S*)-PhMeC(H)OSi(C_6H_5)$_2$H, 79201-73-3; (*R*)-PhEtC(H)OSi(C_6H_5)$_2$H, 55630-28-9; (*S*)-PhEtC(H)OSi(C_6H_5)$_2$H, 79201-74-4; (*R*)-EtMeC(H)OSi(C_6H_5)$_2$H, 79201-75-5; (*S*)-EtMeC(H)OSi(C_6H_5)$_2$H, 79201-76-6; (*R*)-*t*-BuMeC(H)OSi(C_6H_5)$_2$H, 55630-29-0; (*S*)-*t*-BuMeC(H)OSi(C_6H_5)$_2$H, 79201-77-7; (−)-*t*-Bu(*i*-Pr)C(H)OSi(C_6H_5)$_2$H, 79201-78-8; (+)-*t*-Bu(*i*-Pr)C(H)OSi(C_6H_5)$_2$H, 79201-79-9; [RhCl(C_2H_4)$_2$]$_2$, 12081-16-2; [Rh(C_7H_8)$_2$]ClO_4, 60576-58-1; (*S*)-*N*,*N*-dimethyl-1-phenylethylamine, 17279-31-1; (*R*)-*N*,*N*-dimethyl-1-phenylethylamine, 19342-01-9; As(C_6H_5)$_2$Cl, 712-48-1; P(C_6H_5)$_2$Cl, 1079-66-9; (C_6H_5)$_2SiH_2$, 775-12-2; (*R*)-$C_2H_5CHCH_3OH$, 14898-79-4; *cis*-[Rh(*R*-amphos)Cl]$_2$, 79254-35-6; *trans*-[Rh(*R*-amphos)Cl]$_2$, 79201-50-6.

Supplementary Material Available: Listings of hydrogen atom parameters (Table V) and structure amplitudes (11 pages). Ordering information is given on any current masthead page.

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Transition-Metal Complexes of Poly(1-pyrazolyl)borate Ligands. 3.[1] Triphenylphosphine and Di-*p*-tolyl Disulfide Derivatives of Molybdenum and Tungsten (Hydrotris(1-pyrazolyl)borato)dicarbonyl(arenediazo) Complexes and the Crystal and Molecular Structure of (Hydrotris(1-pyrazolyl)borato)bis(*p*-toluenethiolato)(*p*-fluorobenzenediazo)molybdenum(II)

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The complexes HB(pz)$_3$M(CO)$_2$N$_2$Ar react with triphenylphosphine in boiling xylene to yield HB(pz)$_3$M(CO)(PPh$_3$)N$_2$Ar (M = Mo, Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*; M = W, Ar = $C_6H_4CH_3$-*p*) and with di-*p*-tolyl disulfide under similar conditions to give HB(pz)$_3$Mo(SC$_6$H$_4$CH$_3$-*p*)$_2$N$_2$Ar (Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*). The crystal and molecular structure of HB(pz)$_3$Mo(SC$_6$H$_4$CH$_3$-*p*)$_2$(N$_2$C$_6$H$_4$F-*p*), $C_{29}H_{28}BFMoN_8S_2$, is reported. The crystals are monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14) with four molecules in a unit cell of dimensions a = 8.336 (3) Å, b = 33.655 (8) Å, c = 11.063 (2) Å, and β = 95.16 (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculation to $R_F = 0.056$ and $R_{wF} = 0.044$ for 2816 independent reflections (with $I > 3\sigma(I)$) measured by diffractometer. The molybdenum atom has slightly distorted octahedral coordination with Mo–N(arenediazo) = 1.807 (8) Å, Mo–S = 2.328 and 2.344 (3) Å, Mo–N(pyrazolyl) = 2.193–2.234 (8) Å, N–N = 1.229 (9) Å, Mo–N–N = 170.8 (8)°, and N–N–C = 121.4 (9)°. The dimensions establish that the arenediazo ligand is "singly bent" and are interpreted as indicating a considerable degree of double-bond character in the arenediazo Mo–N bond and intermediate between double- and single-bond character in the Mo-S bonds. The chemical behavior of the bis(*p*-toluenethiolato) complexes is briefly reported.

Introduction

In related pairs of carbonyl complexes containing cyclopentadienide and tris(1-pyrazolyl)borate ligands respectively, it is generally found that derivatives of the latter are more resistant to carbonyl displacement than those of the former. This effect may be due to the greater steric bulk of the HB(pz)$_3^-$ ligand restricting access to the metal center or to stabilization of coordinated CO by the more powerfully electron-donating[3] pyrazolylborate ligand or to a combination of both effects. As shown by King and Bisnette,[4] the arenediazo complex (η-C_5H_5)Mo(CO)$_2$(N$_2$C$_6$H$_4$CH$_3$-*p*) yields the monocarbonyl (η-C_5H_5)Mo(CO)(PPh$_3$)(N$_2$C$_6$H$_4$CH$_3$-*p*) when treated with triphenylphosphine in boiling methylcyclohexane (100 °C) and reacts with dimethyl disulfide under similar conditions to give the dinuclear, carbonyl-free [(η-C_5H_5)Mo(μ-SCH$_3$)N$_2$C$_6$H$_4$CH$_3$-*p*]$_2$. In contrast, Trofimenko[5] has reported that the analogous complexes HB(pz)$_3$Mo(CO)$_2$(N$_2$Ar) fail to react with these reagents under similar conditions. We now report that at higher temperatures (xylene, 140 °C) the hydrotris(pyrazolyl)borato complexes will react (albeit very slowly) with triphenylphosphine and di-*p*-tolyl disulfide and describe the complete structural characterization of a novel product of the latter reaction, the *formally* coordinatively unsaturated arenediazo complex HB(pz)$_3$Mo(SC$_6$H$_4$CH$_3$-*p*)$_2$(N$_2$C$_6$H$_4$F-*p*).

Experimental Section

The compounds HB(pz)$_3$Mo(CO)$_2$N$_2$Ar (Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*) and HB(pz)$_3$W(CO)$_2$(N$_2$C$_6$H$_4$CH$_3$-*p*) were prepared by standard literature methods.[5] Other chemicals and solvents were purchased from commercial sources and were used as received. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer and were calibrated with polystyrene film. The 60-MHz ^{1}H NMR spectra were obtained with a Perkin-Elmer/Hitachi R20-A instrument. Microanalyses were carried out by the staff of the Microanalytical Laboratory of the Chemistry Department, University College.

Reaction of HB(pz)$_3$M(CO)$_2$N$_2$Ar (M = Mo, W) with Triphenylphosphine. A solution of HB(pz)$_3$Mo(CO)$_2$(N$_2$C$_6$H$_4$CH$_3$-*p*) (1.0 g, 2.07 mmol) and triphenylphosphine (2.72 g, 10.4 mmol) in 40 mL of xylene was refluxed under nitrogen for 3 days. The solvent was removed in vacuo, and the residue was chromatographed on alumina, eluting with CH_2Cl_2. The first red band to elute yielded a trace of unreacted HB(pz$_3$Mo(CO)$_2$(N$_2$C$_6$H$_4$CH$_3$-*p*) and was followed by a second red band containing the major product of the reaction. Evaporation of the solvent in vacuo and recrystallization of the residue from CH_2Cl_2/hexane gave crystalline HB(pz)$_3$Mo(CO)(PPh$_3$)(N$_2$C$_6$H$_4$CH$_3$-*p*) (0.6 g, 40.5% yield): Ir (CH_2Cl_2) $\bar{\nu}$(CO) 1860 (s) cm^{-1}; $\bar{\nu}$(NN) (assignment tentative in the absence of ^{15}N labeling data) 1530, 1485 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ 8.23 (d, J = 1 Hz, 1 H) 7.80 (m, 3 H), 7.6–7.3 (m, 15 H), 7.0 (d, J = 2 Hz, 1 H), 6.65 (d, J = 2 Hz, 1 H), 6.30 (t, J = 4 Hz, 1 H), 6.10 (s, 4 H), 5.95 (t, J = 4 Hz, 1 H), 5.80 (t, 4 Hz, 1 H), 2.30 (s, 3 H). Anal. Calcd for HB(px)$_3$Mo(CO)(PPh$_3$)(N$_2$C$_6$H$_4$CH$_3$-*p*): C, 58.52; H, 4.46; N, 15.61. Found: C, 58.60; H, 4.47; N, 15.37.

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(1) Part 2: Begley, T.; Condon, D.; Ferguson, G.; Lalor, F. J.; Khan, M. *Inorg. Chem.* **1981**, *20*, 3240.

(2) (a) University College, Cork. (b) University of Guelph.

(3) Carroll, W. E.; Deane, M. E.; Lalor, F. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1837.

(4) King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1966**, *5*, 300.

(5) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 2675.

0020-1669/82/1321-0188$01.25/0

The following compounds were prepared in a similar fashion: $HB(pz)_3Mo(CO)(PPh_3(N_2C_6H_4F\text{-}p)$: 38% yield; IR ($CH_2Cl_2$); $\bar{\nu}$(CO) 1861 (s) cm^{-1}, $\bar{\nu}$(NN) (tentative assignment) 1532, 1486 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 8.15 (d, J = 2 Hz, 1 H), 7.80 (m, 3 H), 7.6–7.3 (m, 15 H), 7.0 (d, J = 2 Hz, 1 H), 6.65 (d, J = 2 Hz, 1 H), 6.30 (t, J = 4 Hz, 1 H), 6.05 (s, 4 H), 5.95 (t, J = 4 Hz, 1 H), 5.80 (t, J = 4 Hz, 1 H). Anal. Calcd: C, 56.53; H, 4.02; N, 15.52. Found: C, 56.50; H, 4.01; N, 15.42. $HB(pz)_3W(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$: 20% yield; IR(($CH_2Cl_2$) $\bar{\nu}$(CO) 1840 (s) cm^{-1}, $\bar{\nu}$(NN) (tentative assignment) 1515, 1486 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si): δ 8.20 (d, J = 2 Hz, 1 H), 7.79 (m, 3 H), 7.6–7.3 (m, 15 H), 6.95 (d, J = 2 HZ, 1 H), 6.64 (d, J = 2 Hz, 1 H), 6.31 (t, J = Hz, 1 H), 6.1 (s, 4 H), 5.94 (t, J = 2 Hz, 1 H), 5.81 (t, J = 2 Hz, 1 H), 2.32 (s, 3 H). Anal. Calcd: C, 52.14; H, 3.97; N, 13.90. Found: C, 52.00; H, 4.01; N, 14.00.

Reaction of $HB(pz)_3Mo(CO)_2(N_2Ar)$ (Ar = $C_6H_4CH_3\text{-}p$, $C_6H_4F\text{-}p$) with $(SC_6H_6CH_3\text{-}p)_2$. A solution of $HB(pz)_3Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ (2.0 g, 4.14 mmol) and di-*p*-tolyl disulfide (4.07 g, 16.5 mmol) in 60 mL of xylene was refluxed under nitrogen for 2 days. Solvent was then removed in vacuo, and the brown residue was subjected to dry-column chromatography on alumina, eluting with CH_2Cl_2. A brown band separated from the origin, and this yielded the brown crystalline product (2.0 g, 72% yield) in analytical purity. Anal. Calcd for $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4CH_3\text{-}p)$: C, 53.43; H, 4.6; N, 16.62. Found: C, 53.40; H, 4.56; N, 16.30. IR (CH_2Cl_2): $\bar{\nu}$(NN) (tentative assignment) 1625, 1582 cm^{-1}; ^1H NMR (CD_2Cl_2, Me_4Si): δ 7.74 (d, J = 1.5 Hz, 2 H), 7.42 (d, J = 1.5 Hz, 1 H), 7.6 (m, 3 H), 6.9 (s, 12 H), 6.11 (t, J = 2 Hz, 2 H), 5.91 (t, J = 2 Hz, 1 H), 2.42 (s, 3 H), 2.24 (s, 6 H). Molecular weight (vapor-phase osmometry in CH_2Cl_2): calcd, 673.8; found, 672.7.

The complex $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$ was prepared similarly in 72% yield. Anal. Calcd: C, 51.34; H, 4.13; N, 16.52. Found: C, 51.00; H, 4.00 N, 16.53. IR (CH_2Cl_2): $\bar{\nu}$(NN) (tentative assignment) 1627, 1583 cm^{-1}. ^1H NMR (CD_2Cl_2, Me_4Si): δ 7.99 (d, J = 4 Hz, 2 H), 7.65 (d, J = 4 Hz, 1 H), 7.79 (m, 3 H), 7.17 (d, J = 14 Hz, 4 H), 7.08 (s, 8 H), 6.29 (t, J = 2 Hz, 2 H), 6.10 (t, J = 2 Hz, 1 H), 2.3 (s, 6 H).

Crystal Structure Analysis. Dark red parallelepiped crystals of $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$ grown from CH_2Cl_2/hexane solution were examined with precession and Weissenberg photographs. Systematic absences $h0l$, when $h + l = 2n + 1$, and $0k0$, when $k = 2n + 1$, define the space group $P2_1/n$ uniquely (an alternate setting of $P2_1/c$ C_{2h}^5, No. 14) with equivalent positions $\pm[x, y, z$ and $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z]$). The unit cell parameters were obtained from a least-squares fit of the θ values of 12 reflections measured on a Hilger & Watts Y290 four-circle diffractometer using a crystal elongated along c with dimensions 0.07 × 0.11 × 0.24 mm.

Crystal data: $HB(C_3H_3N_2)_3Mo(SC_6H_4CH_3)_2(N_2C_6H_4F)$, $C_{29}H_{28}BFMoN_8S_2$; M_r = 678.5; a = 8.336 (3), b = 33.655 (8), c = 11.063 (2) Å; β = 95.16 (1)°; V = 3091.3 Å^3; Z = 4; D_c = 1.46 g cm^{-3}; $F(000)$ = 1384; μ(Mo Kα) = 5.3 cm^{-1}.

Intensity data in the range 1° < θ < 25° were collected with a Hilger & Watts Y290 computer-controlled diffractometer using the θ–2θ scan technique and monochromated Mo Kα radiation as described previously.[6] A symmetric scan range of 0.6° in θ was composed of 60 steps of 1-s duration. Stationary crystal–stationary counter background counts of 15 s were made at the beginning and end of each scan. The intensities of three standard reflections, monitored at 100-reflection intervals, did not change significantly over the period of the data collection.

A total of 5440 intensity maxima were collected and corrected for Lorentz, polarization, and absorption effects;[7] the maximum and minimum values of transmission coefficients are 0.96 and 0.94. Of the 4932 unique reflections, the 2816 with $I > 3\sigma(I)$ were labeled observed and used in all subsequent calculations. The structure was solved via the heavy-atom method. The coordinates of the molybdenum atom were obtained from a three-dimensional Patterson synthesis and those of the nonhydrogen atoms from a subsequent Fourier synthesis. Refinement by full-matrix least-squares calculations using unit weights initially with isotropic and then anisotropic thermal parameters lowered R_F to 0.065. A difference synthesis at this stage showed electron density maxima 0.3–0.6 e Å^{-3} in positions expected for the hydrogen atoms; no other chemically significant maxima were observed. The atomic scattering curves for the nonhydrogen atoms were taken from ref 8 and that for hydrogen from ref 9, and allowance was made for anomalous dispersion.[10] The refinement continued with allowance being made for the hydrogen atoms (in chemically expected positions with C–H = 0.95 Å and an overall U_{iso} value of 0.09 Å^2) and with weights derived from the counting statistics. In three more cycles refinement had converged completely with R_F = 0.056 and R_{wF} = $(\sum w\Delta^2/\sum wF_o^2)^{1/2}$ = 0.044. In the final cycle, the maximum coordinate shift/error ratio was 0.40 for the z coordinate of N(41), and a final difference synthesis showed no significant features.

Table I. Final Fractional Coordinates for $HB(pz)_3Mo(N_2C_6H_4F)(SC_6H_4CH_3)_2$ (×10^5 for Mo; ×10^4 for Remainder) with Estimated Standard Deviations in Parentheses

atom	x	y	z
Mo	6971 (8)	11224 (2)	17169 (5)
S(1)	−411 (2)	663 (1)	2978 (2)
S(2)	158 (3)	1753 (1)	2488 (2)
F	6621 (8)	1840 (2)	7138 (5)
N(1)	2668 (7)	1119 (2)	2543 (5)
N(2)	4040 (8)	1066 (2)	3022 (5)
N(41)	1335 (7)	628 (2)	563 (5)
N(42)	785 (7)	596 (2)	−621 (5)
N(51)	−1669 (7)	1068 (2)	609 (5)
N(52)	−1728 (8)	998 (2)	−612 (5)
N(61)	1471 (7)	1408 (2)	71 (5)
N(62)	876 (8)	1307 (2)	−1068 (5)
B	−234 (11)	947 (3)	−1256 (8)
C(11)	4648 (9)	1288 (2)	4059 (6)
C(12)	6155 (10)	1169 (2)	4566 (7)
C(13)	6812 (11)	1358 (3)	5615 (9)
C(14)	5980 (16)	1657 (3)	6104 (8)
C(15)	4519 (13)	1786 (3)	5597 (8)
C(16)	3859 (10)	1601 (2)	4553 (7)
C(21)	1018 (8)	506 (2)	4171 (6)
C(22)	1573 (9)	120 (2)	4209 (7)
C(23)	2684 (10)	−9 (3)	5128 (8)
C(24)	3246 (11)	250 (3)	6065 (8)
C(25)	2646 (10)	624 (3)	6029 (7)
C(26)	1569 (10)	757 (2)	5110 (7)
C(27)	4471 (11)	95 (3)	7059 (7)
C(31)	−1659 (11)	1968 (2)	1832 (8)
C(32)	−2886 (10)	2052 (2)	2516 (8)
C(33)	−4213 (11)	2273 (2)	2089 (8)
C(34)	−4307 (11)	2417 (2)	907 (8)
C(35)	−3143 (12)	2327 (3)	205 (9)
C(36)	−1800 (12)	2111 (3)	628 (8)
C(37)	−5695 (12)	2681 (3)	449 (9)
C(41)	2251 (9)	311 (2)	820 (6)
C(42)	2275 (10)	64 (2)	−166 (8)
C(43)	1349 (10)	258 (2)	−1054 (6)
C(51)	−3175 (10)	1080 (2)	918 (7)
C(52)	−4243 (10)	1014 (2)	−105 (9)
C(53)	−3288 (10)	969 (2)	−1047 (8)
C(61)	2500 (10)	1712 (2)	−76 (8)
C(62)	2540 (13)	1807 (3)	−1312 (8)
C(63)	1498 (12)	1540 (3)	−1874 (7)

Final fractional coordinates for the atoms are in Table I, and details of molecular dimensions are in Table II. A view of the molecule with the crystallographic numbering scheme is in Figure 1, and a stereoscopic view of the molecular packing is in Figure 2. Lists of anisotropic thermal parameters, calculated hydrogen coordinates, and observed and calculated structure factors are available.[11]

Results and Discussion

The complexes $HB(pz)_3Mo(CO)_2N_2Ar$ (Ar = $C_6H_4CH_3\text{-}p$, $C_6H_4F\text{-}p$) and $HB(pz)_3W(CO)_2(N_2C_6H_4CH_3\text{-}p)$ were treated with a fivefold excess of triphenylphosphine in xylene at 140

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(6) Restivo, R. J.; Ferguson, G.; Ng, T. W.; Carty, A. J. *Inorg. Chem.* **1977**, *16*, 172.

(7) All numerical calculations were done with the SHELX system of programs: G. M. Sheldrick, University Chemical Laboratories, Cambridge, CB2 1EW, England.

(8) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(9) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(10) Cromer, D. T.; Liberman, D. L. *J. Chem. Phys.* **1970**, *53*, 1891.

(11) Supplementary material.

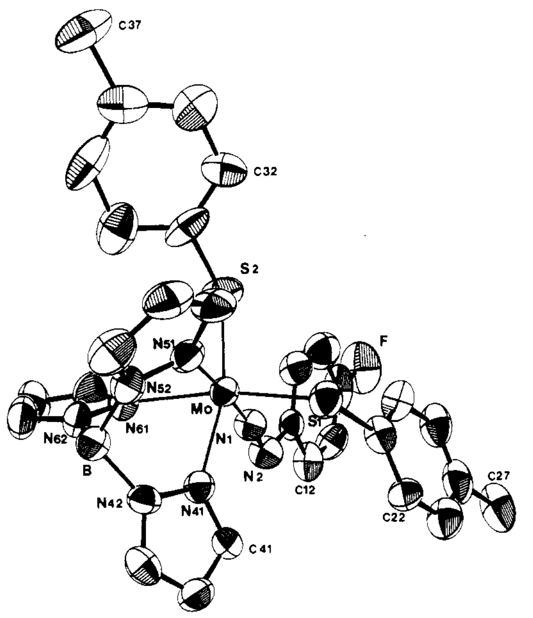
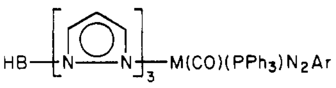


Figure 1. View of the $HB(pz)_3Mo(N_2C_6H_4F)(SC_6H_4CH_3)_2$ molecule with the crystallographic numbering scheme.

°C. Monitoring of the reaction by IR spectroscopy showed a slow decrease in intensity of the two carbonyl bands characteristic of the starting material and their replacement by a single strong $\bar{\nu}(CO)$ band at lower wave number. This process was complete after ca. 3 days. Workup of the reaction mixture yielded stable red solids in ca. 20–40% yield which were assigned the structures I and II, respectively.



I, M = Mo, Ar = $C_6H_4CH_3$-*p*, C_6H_4F-*p*
II, M = W, Ar = $C_6H_4CH_3$-*p*

Microanalytical, IR, and ^1H NMR data for I and II (Experimental Section) are in agreement with the proposed structure. The complexes show a single strong $\bar{\nu}(CO)$ band which is displaced ca. 90–100 cm^{-1} to lower wavenumber from the average position of $\bar{\nu}(CO)$ in their dicarbonyl precursors. The IR bands tentatively assigned to $\bar{\nu}(NN)$ in I and II are similarly shifted with respect to the dicarbonyl compounds,[3] but this observation is subject to confirmation by ^{15}N labeling studies. The most significant feature of the ^1H NMR spectra of I and II is the observation in each case of three well-resolved

Table II. Principal Interatomic Distances (Å) and Angles (Deg) in $HB(pz)_3Mo(N_2C_6H_4F)(SC_6H_4CH_3)^a$ with Estimated Standard Deviations in Parentheses

Mo-S(1)	2.328 (3)	N(51)-C(51)	1.331 (12)
Mo-S(2)	2.344 (3)	N(52)-C(53)	1.349 (12)
Mo-N(1)	1.807 (8)	N(52)-B	1.499 (14)
Mo-N(41)	2.193 (8)	N(61)-N(62)	1.356 (10)
Mo-N(51)	2.234 (8)	N(61)-C(61)	1.354 (12)
Mo-N(61)	2.206 (8)	N(62)-C(63)	1.328 (10)
S(1)-C(21)	1.777 (9)	N(62)-B	1.527 (14)
S(2)-C(31)	1.775 (11)	C(14)-F	1.366 (13)
N(1)-N(2)	1.229 (9)	C(41)-C(42)	1.37 (1)
N(2)-C(11)	1.423 (12)	C(42)-C(43)	1.36 (1)
N(41)-N(42)	1.352 (9)	C(51)-C(52)	1.39 (1)
N(41)-C(41)	1.326 (11)	C(52)-C(53)	1.38 (1)
N(42)-C(43)	1.337 (11)	C(61)-C(62)	1.41 (1)
N(42)-B	1.582 (13)	C(62)-C(63)	1.36 (1)
N(51)-N(52)	1.367 (9)		

S(1)-Mo-S(2)	106.4 (1)	Mo-N(41)-N(42)	123.0 (6)
S(1)-Mo-N(1)	94.9 (3)	Mo-N(41)-C(41)	130.5 (6)
S(1)-Mo-N(41)	88.6 (2)	N(42)-N(41)-C(41)	106.5 (7)
S(1)-Mo-N(51)	84.1 (2)	N(41)-N(42)-C(43)	108.3 (8)
S(1)-Mo-N(61)	160.9 (2)	N(41)-N(42)-B	119.6 (8)
S(2)-Mo-N(1)	91.0 (3)	C(43)-N(42)-B	132.0 (8)
S(2)-Mo-N(41)	164.4 (2)	Mo-N(51)-N(52)	120.5 (6)
S(2)-Mo-N(51)	94.9 (2)	Mo-N(51)-C(51)	131.5 (7)
S(2)-Mo-N(61)	89.2 (2)	N(52)-N(51)-C(51)	107.9 (8)
N(1)-Mo-N(41)	91.9 (3)	N(51)-N(52)-C(53)	108.2 (8)
N(1)-Mo-N(51)	174.2 (3)	N(51)-N(52)-B	122.1 (8)
N(1)-Mo-N(61)	95.7 (3)	C(53)-N(52)-B	129.6 (9)
N(41)-Mo-N(51)	82.4 (3)	Mo-N(61)-N(62)	123.3 (6)
N(41)-Mo-N(61)	75.3 (3)	Mo-N(61)-C(61)	131.5 (8)
N(51)-Mo-N(61)	83.8 (3)	N(62)-N(61)-C(61)	105.1 (8)
Mo-S(1)-C(21)	111.5 (3)	N(61)-N(62)-C(63)	110.1 (9)
Mo-S(2)-C(31)	113.9 (3)	N(61)-N(62)-B	119.5 (8)
Mo-N(1)-N(2)	170.8 (8)	C(63)-N(62)-B	130.3 (9)
N(1)-N(2)-C(11)	121.4 (9)	N(61)-C(61)-C(62)	111.0 (11)
N(41)-C(41)-C(42)	111.4 (9)	C(61)-C(62)-C(63)	103.0 (10)
C(41)-C(42)-C(43)	103.7 (9)	N(62)-C(63)-C(62)	110.8 (10)
N(42)-C(43)-C(42)	110.1 (9)	N(42)-B-N(52)	108.1 (8)
N(51)-C(51)-C(52)	109.6 (10)	N(42)-B-N(62)	103.7 (8)
C(51)-C(52)-C(53)	105.2 (10)	N(52)-B-N(62)	111.3 (9)
N(52)-C(53)-C(52)	109.1 (10)		

[a] Lists of the other bond lengths and angles are available.[11] Mean dimensions include phenyl C-C = 1.38 (2) Å and $C(sp^2)$-C(methyl) = 1.52 (2) Å.

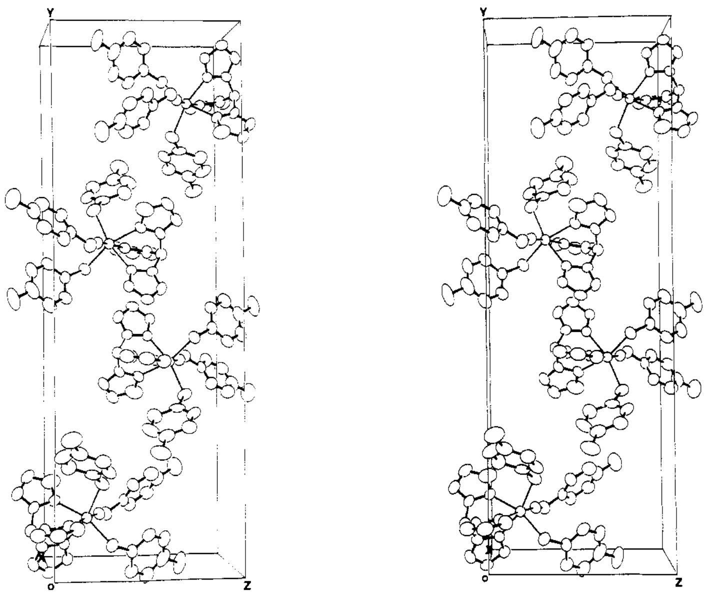
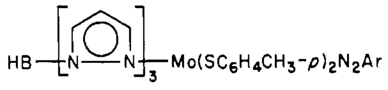


Figure 2. Stereoscopic view of four molecules in the unit cell of $HB(pz)_3Mo(N_2C_6H_4F)(SC_6H_4CH_3)_2$.

triplets at ca. δ 5.8, 5.9 and 6.8, respectively, each corresponding to a single proton. These are assigned to the hydrogen atoms at position 4 of the three pyrazolyl groups in the coordinated $HB(pz)_3^-$ ligand. An octahedral structure is indicated for I and II with a rigid nonrotating tris(1-pyrazolyl)borato ligand and three inequivalent pyrazolyl groups *trans* to CO, PPh_3, and N_2Ar, respectively. The isolation and stability of I and II show that the Mo(0) (and W(0)) coordination spheres can simultaneously accommodate the bulky hydrotris(pyrazolyl)borato and triphenylphosphine ligands without undue steric crowding. That the reduced reactivity of $HB(pz)_3Mo(CO)_2Ar$ vis-a-vis $(\eta\text{-}C_5H_5)Mo(CO)_2N_2Ar$ is likely to result from inhibition of CO dissociation by the more strongly electron-releasing pyrazolylborato ligand rather than from steric effects is in line with this observation, but a kinetic study will be required to provide a definitive solution to this problem.

Trofimenko[5] reports that complexes of the type $HB(pz)_3Mo(CO)_2N_2Ar$ are unaffected by refluxing with dimethyl disulfide but does not specify the precise reaction conditions. We found that $HB(pz)_3Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$ does react with excess dimethyl disulfide in boiling xylene but could not isolate any characterizable organometallic products. However, under similar conditions, $HB(pz)_3Mo(CO)_2N_2Ar$ (Ar = $C_6H_4CH_3\text{-}p$, $C_6H_4F\text{-}p$) reacted smoothly with di-*p*-tolyl disulfide, and after ca. 2 days the IR spectrum of the reaction mixture indicated that both carbonyl groups had been displaced. Workup of the reaction mixture yielded dark red crystalline solids which showed no sign of decomposition after exposure to the atmosphere for extended periods of time in the solid state or in solution in polar organic solvents. These complexes were expected to have the structure $[HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)N_2Ar]_2$ by analogy with the corresponding reaction in the cyclopentadienyl series.[4] Microanalytical and ^1H NMR data did not support this formulation but indicated instead that the new complexes had structure III. The ^1H NMR spectrum of the compounds of type III



III, Ar = $C_6H_4CH_3\text{-}p$, $C_6H_4F\text{-}p$

showed a pair of triplets due to pyrazolyl 4-hydrogens in the δ 5.9–6.3 region corresponding to one and two protons, respectively. The observed pattern is consistent with octahedral coordination around molybdenum and a local symmetry plane which includes one pyrazolyl group and the arenediazo ligand while bisecting the solid angles between the other two pyrazolyl groups and the two *p*-toluenethiolato ligands. A molecular weight determination of III (Ar = $C_6H_4CH_3\text{-}p$) indicated that the species was monomeric in CH_2Cl_2 solution. The mass spectrum of III (Ar = $C_6H_4CH_3\text{-}p$) indicated that the compound was also monomeric in the vapor phase. The parent molecular ion was observed at *m/e* 676 ($^{12}C_{30}{}^1H_{31}{}^{11}B^{98}Mo^{14}N_8{}^{32}S_2$) as the second most intense peak in the mass spectrum. Fragmentation was initially by loss of $N_2C_7H_7$ and SC_7H_7 groups, giving abundant ions corresponding to $[P - N_2C_7H_7]^+$, $[P - SC_7H_7]^+$, and $[P - N_2C_7H_7 - SC_7H_7]^+$. The base peak was due to $[Mo(SC_7H_7)_2 - H]^+$. Formation of the base peak ion from P^+ via successive loss of $N_2C_7H_7$ and $H_2B(C_3H_3N_2)_3$ was supported by the observation of metastable peaks (m^*: theory 458.9, 211.2; found 458.7, 211.0). Ions not containing metal atoms were observed corresponding to $[(SC_7H_7)_2]^+$, $[H_2B(C_3H_3N_2]^+$, $[SC_7H_8]^+$, $[SC_7H_7]^+$, and $[C_7H_7]^+$.

Arenediazobis(thiolato) complexes of type III are of structural interest for several reasons. First, they may have some general relevance to intermediates involved in biological nitrogen fixation since the dinitrogen-binding molybdenum sites in nitrogenase are thought to be coordinated by up to five sulfur ligands.[12] Second, a monomeric structure for III implies a *formal* coordinatively unsaturated (16-electron) Mo(II) center [with the assumption that $HB(pz)_3^-$ is tridentate, that the arenediazo ligand is a cationic two-electron donor (i.e., singly bent $[ArN_2]^+$), and that the arenethiolato ligands each donate two electrons to the metal atom]. However, the stability of III is unexpected for a 16-electron Mo(II) complex and raises the possibility that the metal atom might achieve effective coordinative saturation via p_π–d_π electron donation from the sulfur atoms of one or both thiolato ligands. We have previously observed molybdenum–thiolato sulfur multiple bonding of this type in $HB(Me_2pz)_3Mo(SC_6H_4Cl\text{-}p)(CO)_2$.[1] McCleverty and his co-workers[13] have established the presence of similar p_π–d_π donation from a ligating oxygen atom in an alkoxo–halide complex formally related to III, i.e. $HB(3,5\text{-}Me_2\text{-}4\text{-}Clpz)_3MoCl(OC_3H_7\text{-}i)NO$. We have therefore carried out a single-crystal X-ray diffraction study of III (Ar = $C_6H_4F\text{-}p$) in order to establish the general structural features of the complex and to determine whether the formal electron deficiency at molybdenum is removed by multiple bonding from the thiolato ligands.

Crystals of $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$ contain discrete monomeric molecules (Figure 2) that are separated by normal van der Waals distances. The coordination about the molybdenum atom (Figure 1) is slightly distorted octahedral with pyrazolyl N–Mo–N = 75.3–83.8 (3)° as a consequence of the "bite" of the $HB(pz)_3^-$ ligand. The Mo–N(pyrazolyl) bond length 2.234 (8) Å (trans to arenediazo-N) is barely significantly longer than those trans to S (2.193 and 2.206 (8) Å); significant differences (~0.05 Å) in Mo–N(pyrazolyl) bonds attributable to trans effects have been observed previously, e.g., in $HB(Me_3pz)_3Mo(SC_6H_4CH_3\text{-}p)(CO)_2$[1] and in $PhB(pz)_3Mo_3Mo(CO)_2C_7H_7$.[14] The dimensions within the organic structures of the hydrotris(pyrazolyl)borato and thiolato ligands are unexceptional and in accord with accepted values: mean phenyl C–C = 1.38 (2), C(sp^2)–C(methyl = 1.52 (2), pyrazolyl C–C 1.38 (1), pyrazolyl C–N = 1.34 (1), pyrazolyl N–N = 1.36 (1), and N–**B** = 1.54 (1) Å.

The arenediazo ligand has an Mo–N(1)–N(2) angle of 170.8 (8)° and N(1)–N(2)–C(11) = 121.4 (9)°, allowing the geometry to be classified as "singly bent". The Mo–N(1) distance (1.807 (8) Å) is comparable to the corresponding bond in $MoCl(N_2COPh)(NHNCOPh)(PMe_2Ph)_2$,[15] (1.78 (1) Å) and shorter than those reported for $(\eta^5\text{-}CH_3C_5H_4)MoCl(N_2C_6H_4F)_2$[16] (1.826 (2) and 1.834 (3) Å) and for $HB(pz)_3Mo(CO)_2N_2C_6H_5$[17] (1.825 (4) Å). The N–N distance (1.229 (9) Å) is also within the range previously established for the "singly bent" coordination mode. The *p*-fluorobenzenediazo ligand in III is therefore clearly to be regarded as a two-electron donor (formal $[ArN_2]^+$) with strong back-donation from the metal to the ligand N–N π^* orbitals.

While significantly longer than Mo═S (terminal sulfido) bonds (2.10 (2) Å),[18] the bonds between molybdenum(II) and

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(12) Cramer, S. D.; Hodgson, K. O.; Stiefel, E. I.; Newton, W. E. *J. Am. Chem. Soc.* **1978**, *100*, 2748.

(13) McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. J. *J. Chem. Soc., Dalton Trans.* **1976**, 898.

(14) Cotton, F. A.; Murillo, C. A.; Stults, B. R. *Inorg. Chim. Acta* **1977**, *22*, 75.

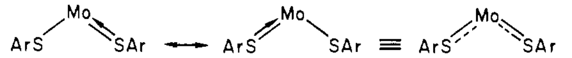
(15) Butcher, A. V.; Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Hursthouse, M. B.; Amarasiri, S.; Jayaweera, A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 921.

(16) Lalor, F. J.; Condon, D.; Ferguson, G.; Khan, M. *Inorg. Chem.* **1981**, *20*, 2178.

(17) Avitabile, G.; Ganis, P.; Nemiroff, M. *Acta Crystallogr., Sect. B* **1971**, *B27*, 725.

(18) See: Hunecke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698 and references therein.

thiolato sulfur in III (Ar = C_6H_4F-*p*) (2.328 (3) and 2.344 (8) Å) are intermediate in length between Mo—SR(thiolato) single bonds (2.45 Å)[18] and the molybdenum–sulfur distance found in the Mo(II) monothiolato complex $HB(Me_2pz)_3Mo(SC_6H_4Cl\text{-}p)(CO)_2$ (2.305 (1) Å).[1] In the latter complex, a full p_π–d_π bond between molybdenum and thiolato sulfur is required if the molybdenum atom is to attain an 18-electron configuration. We interpret this intermediate character of the Mo–S(thiolato) bonds in III as indicating the *both* sulfur atoms participate equally in p_π–d_π interaction with molybdenum so that the latter attains an effective closed valence-shell via a combination of two reasonance structures:



The individual thiolato ligands in III may therefore be regarded as formal 2.5-electron donors. The Mo–S–C angles (111.5 (3) and 113.9 (3)°) are intermediate between those found[19] in (*o*-(phen)Zn$(SC_6H_4CH_3\text{-}p)_2$ (104.6 and 95.9 (2)°), where the metal–S bonding is presumably purely σ, and in $HB(Me_2pz)_3Mo(SC_6H_4Cl\text{-}p)(CO)_2$ (116.5 (1)°), where there is strong p_π–d_π bonding.[1]

Analogy with the known chemistry of bis(thiolato) complexes such as $(\eta\text{-}C_5H_5)_2M(SR)_2$ (M = Ti, Mo, W)[20] suggested that compounds of type III should behave as chelating (2 + 2)-electron ligand via lone pairs of the thiolato sulfur atoms. However, no evidence for formation of $HB(pz)_3Mo(N_2C_6H_4CH_3\text{-}p)(\mu\text{-}SC_6H_4CH_3\text{-}p)_2Mo(CO)_4$ was observed when complex III (Ar = $C_6H_4CH_3$-*p*) was treated with (norbornadiene)molybdenum tetracarbonyl in benzene and the reactants were recovered unchanged. Reaction did take place between the bis(thiolato) complex and $(C_6H_5CN)_2PdCl_2$ in CH_2Cl_2, but the scarlet product—possibly $HB(pz)_3Mo(N_2C_6H_4CH_3\text{-}p)(\mu\text{-}SC_6H_4CH_3\text{-}p)_2PdCl_2$—decomposed before characterization could be attempted. Neither was it possible to generate seven-coordinate 18-electron anionic species such as $[HB(pz)_3MoCl(SC_6H_4CH_3\text{-}p)_2N_2Ar]^-$ via the reaction of III with halide salts in CH_2Cl_2.

Acknowledgment. This work was supported by a Maintence Award from the Department of Education of the Republic of Ireland (to D.C.) and by the National Research Council of Canada (to G.F.). We are grateful to Dr. N. M. Connelly of the Department of Inorganic Chemistry, Bristol University, for the molecular weight and mass spectroscopic data.

Registry No. $HB(pz)_3Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$, 79329-42-3; $HB(pz)_3Mo(CO)(PPh_3)(N_2C_6H_4F\text{-}p)$, 79329-43-4; $HB(pz)_3W(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$, 79329-44-5; $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4CH_3\text{-}p)$, 79329-45-6; $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$, 79357-02-1; $HB(pz)_3Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$, 53158-54-6; $HB(pz)_3Mo(CO)_2(N_2C_6H_4F\text{-}p)$, 53158-57-9; $HB(pz)_3W(CO)_2(N_2C_6H_4CH_3\text{-}p)$, 79329-46-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, molecular dimensions not included in Table II, calculated hydrogen coordinates, and structure factors (23 pages). Ordering information is given on any current masthead page.

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[19] Cremers, T. L.; Bloomquist, D. R.; Willett, R. D.; Crosby, G. A. *Acta Crystallogr., Sect. B* **1980**, *B36*, 3097.

[20] Dias, A. R.; Green, M. L. H. *J. Chem. Soc. A* **1971**, 2807 and references therein.

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Preparation, Unusual Spectral Properties, and Structural Characterization of (Terpyridine)(tetrahydroborato-*H*,*H'*)cobalt

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A new compound of cobalt possessing terpyridine and tetrahydroborato ligands has been prepared by reduction of $[Co(terpy)Cl_2]$ with $NaBH_4$. Single-crystal X-ray and neutron diffraction studies have established the molecular structure of the compound. The coordination sphere of the cobalt can be described as a distorted tetragonal pyramid in which the apex and one basal vertex are occupied by bridging hyrides of the bis-chelate tetrahydroborato ligand. The infrared spectrum of the molecule displays features at variance with those anticipated for a complex with a bis-chelate tetrahydroborato ligand, and we suggest that caution should be exercised in the use of infrared spectroscopy for the structural characterization of tetrahydroborato complexes. Crystallographic details: $C_{15}H_{15}N_3CoB$, space group $P2_1/c$, Z = 4, *a* = 8.173 (1) Å, *b* = 15.802 (5) Å, *c* = 10.708 (4) Å, β = 92.84 (2)° (*T* = 298 K); *a* = 8.038 (3) Å, *b* = 15.701 (5) Å, *c* = 10.593 (3) Å, β = 94.03 (3)° (*T* = 50 K). Final *R*(*F*) values are 0.047 for 2718 X-ray reflections measured at 298 K and 0.062 for 1497 neutron reflections measured at 50 K.

Introduction

The reactivity of the square-planar cation $[Co(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^+$ (**1**) and its congeners toward oxidative addition of H_2 has been reported to decrease in the order Co > Rh > Ir.[2] This suggests that neutral square-planar cobalt(I) complexes, isotypic with Wilkinson's catalyst and Vaska's complex, might be sufficiently reactive oxidative addition substrates to activate sp^3 C–H bonds in a manner reminiscent of the isoelectronic reactive intermediate $[Fe((CH_3)_2PCH_2CH_2P(CH_3)_2)_2]$.[3] Our interest in this area was stimulated by the interest of some of us in the mechanisms of B_{12}-mediated enzymic reactions that led us to suggest the possibility that square-planar cobalt(I) species might be the active species in such reactions.[4] The work reported in this paper represents an attempt to test this hypothesis by the study of appropriate model compounds.

Although the vast majority of four-coordinate cobalt(I) complexes adopt high-spin tetrahedral configurations,[5] both **1** and $[Co(Ph_2PCH_2CH_2PPh_2)_2]^{+}$[6] are known to be low-spin, square-planar complexes. This is presumably a consequence

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[1] (a) Harvard University. (b) Brookhaven National Laboratory.

[2] Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

[3] Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 6073.

[4] Corey, E. J.; Cooper, N. J.; Green, M. L. H. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 811.

[5] Aresta, M.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* **1969**, *3*, 227.

[6] Sacco, A.; Rossi, M.; Nobile, C. F. *Chem. Commun.* **1966**, 589.

0020-1669/82/1321-0192$01.25/0