Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.

Complexes of Polypyrazolylborate Ligands. VII.[1] X-Ray Crystal Structure of a Complex Containing Both a Unidentate Pyrazole Ligand and a Bidentate Pyrazolylborate Ligand: (Diethylbispyrazolylborato)(pyrazylato)(trihaptoallyl)(dicarbonyl)molybdenum[2]

F. Albert Cotton,[3] Bertram A. Frenz, and Anna G. Stanislowski

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The crystal structure of (diethylbispyrazolylborato) (pyrazylato) (trihaptoallyl) (dicarbonyl)molybdenum, $[Et_2B(pz)_2]$ $(\eta^3\text{-}C_3H_5)(Hpz)(CO)_2Mo$, crystallizes in the space group $P2_1/n$. Unit cell dimensions are a = 8.144(2), b = 13.833(3), c = 18.792(3) Å, β = 93.49(2)°; the density (by flotation) = 1.46 g cm^{-3}; calculated (for Z = 4) 1.459 g cm^{-3}. The intensities of 2948 independent reflections were collected with Mo Kα radiation on a Syntex $P\bar{1}$ diffractometer. The structure was solved by the usual Patterson and Fourier methods and refined by full-matrix least-squares methods to final unweighted and weighted residuals of 0.027 and 0.037, respectively. The coordination geometries of the molybdenum and the boron atoms are distorted octahedral and tetrahedral, respectively. The N-N distances are 1.367(4) Å for the pyrazolylborate and 1.348(4) Å in the pyrazole, with the Mo-N distances being 2.238(3) Å and 2.237(3) Å. The nonbonded distance between the Mo and the boron is 3.806(4) Å, approximately 1.0 Å longer than the respective distances in the $[H_2B(Me_2pz)_2]$ $(\eta^3\text{-}C_7H_7)$-$(CO)_2Mo$ and $[H_2B(Me_2pz)_2]$ $(\eta^3\text{-}C_3H_5)(CO)_2Mo$ molecules.

Introduction

A number of transition metal complexes with pyrazolylborate have been studied in recent years.[4,5] Studies on structures with an apparent 16-electron configuration at the molybdenum, $[H_2B(Me_2pz)_2](\eta^3\text{-}C_7H_7)(CO)_2Mo$,[5] and $[H_2B(Me_2pz)_2](\eta^3\text{-}C_3H_5)(CO)_2$-Mo,[6] have shown that the six-membered ring formed by the Mo atom, the four nitrogen atoms, and the boron atom, assumes a very pronounced boat conformation in order to bring the hydrogen on the boron atom within the orbital sphere of the molybdenum atom. This allows the molybdenum atom to achieve a closed valence shell configuration, by participating in a 2-electron, 3-center B-H-Mo bond. We wished to study the related compound $[Et_2B(pz)_2]$-$(\eta^3\text{-}C_3H_5)(CO)_2Mo$ to see if an alpha hydrogen atom of an ethyl group might play a role similar to that of the hydrogen atom from boron in the aforementioned compounds.

The diethylbispyrazolylborato compound is considerably less stable than the dihydro compounds and showed little tendency to form good crystals. After prolonged efforts to crystallize the substance, we at last found a single well-formed crystal. The quantity of crystalline material was too small to allow spectroscopic or analytical characterization. Despite some misgivings about the identity of the crystalline substance, based on the fact that it had a distinctly lighter color than the bulk of the microcrystalline diethyl compound, a single crystal x-ray structural study was undertaken.

The structural investigation showed, at an early stage, that we did not, in fact, have crystals of the desired molecule, but rather of its pyrazole adduct. Prior to the first attempts to obtain crystals, the compound had been purified chromatographically and should thus have been free of the pyrazole adduct. Presumably, in the course of our extended efforts to grow crystals some decomposition occurred and free pyrazole was generated. This free pyrazole, exactly as would be expected, then reacted with some of the starting material to generate the already known pyrazole adduct. Since this substance had a certain degree of interest, though not so much as the starting material, and because a good data set was already in hand, it was decided to refine the structure which had been solved. That structure is reported here.

Experimental Section

Diethylbis(1-pyrazolyl)borato-η³-allyldicarbonylmolybdenum, $[Et_2B(pz)_2](\eta^3\text{-}C_5H_5)(CO)_2Mo$, was prepared by Dr. A. Shaver according to Trofimenko's method.[7] Repeated attempts to recrystallize this sample from ether, pentane, hexane, toluene, CS_2-hexane

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[3] Address correspondence to this author.

[4] See S. Trofimenko, *Chem. Rev.*, 72, 497 (1972) and the references therein.

[5] F.A. Cotton, M. Jeremic, and A. Shaver, *Inorg. Chim. Acta*, 6, 543 (1972).

[6] C.A Kosky, P. Ganis, and G. Avitabile, *Acta Crystallogr.*, Sect. B, 27, 1859 (1971).

[7] S. Trofimenko, *J. Amer. Chem. Soc.*, 90, 4754 (1968); *Inorg. Chem.*, 9, 2493 (1970).

(1:1), CS_2-pentane (1:1), and toluene-hexane (1:5) produced only orange needle-shaped crystals whose Laue photographs were heavily streaked. Several of these crystals were examined on the diffractometer; the omega scans of various reflections showed asymmetric peaks having widths at half-height varying from 0.5 to 0.7°.

However, a methylcyclohexane solution gave one yellow tabular crystal of dimensions 0.36×0.30×0.12 mm. This crystal was examined on a Syntex P$\bar{1}$ computer-controlled four-circle diffractometer and found to belong to the monoclinic system with cell constants of a = 8.144(2), b = 13.833(3), c = 18.792(2) Å, and β = 93.49(2)°, as determined from least-squares refinement of the setting angles for fifteen reflections with 2θ values greater than 40°. For V = 2113.1(8) $Å^3$, mol. wt. = 464.19, and Z = 4, the calculated density is 1.46 g cm^{-3}. A narrower (0.17°) and more symmetric peak was observed for ω scans of several strong reflections.

Data were collected at 20±1° using Mo Kα radiation monochromatized with a graphite crystal. The θ-2θ scan technique with a variable scan rate from 2.0 to 24.0°/min and a scan range from 2θ (Mo $K\alpha_1$) − 0.8° to 2θ (Mo $K\alpha_2$) + 0.8° was used to collect 2948 independent data up to a maximum 2θ value of 45°. Instrument and crystal stability were monitored by measuring the intensities of four reflections, widely separated in reciprocal space, after every 50 reflections; no significant variation was observed. Additional details on the data collection procedure have been given previously.[8]

The intensities were reduced to relative amplitudes, $|F_o|$, by means of standard Lorentz and polarization corrections. The linear absorption coefficient of the compound is 6.4 cm^{-1}. No absorption correction was made. Of the 2948 unique reflections collected, 652 were rejected as unobserved by applying the criterion that $F_o^2 < 3.0\sigma(F_o^2)$, where $\sigma(F_o^2)$ is the standard deviation on the intensity. The parameter p used in the calculation of standard deviations was set equal to 0.05.[8]

Solution and Refinement[9]

A three-dimensional Patterson function based on 1120 reflections (2θ < 30°) revealed the position of the molybdenum atom. Its coordinates were refined in a least-square cycle and this was followed by a difference Fourier synthesis to give the positions of four N atoms, a C atom, and an O atom. The remaining atoms were found from subsequent least-squares and difference Fourier procedures. The agreement factors after isotropic refinement of all the non-hydrogen atoms using the 1120 low angle data were $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.068$ and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.11$.

The quantity minimized in the least-squares refinement is $\Sigma w(|F_o|-|F_o|)^2$, where $|F_o|$ and $|F_c|$ are respectively the observed and the calculated structure factor amplitudes and the weight $w = 4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from Cromer and Waber.[10] The anomalous dispersion correction for Mo employed Δf′ and Δf″ values from Cromer and Liberman.[11] Two least-squares cycles including anisotropic thermal parameters reduced the residual values to $R_1 = 0.048$ and $R_2 = 0.077$. The geometric positions of the hydrogen atoms were then calculated and in subsequent calculations, based on the whole data set, their contribution was included in the structure factors but their coordinates and temperature factors (B = 4.0) were held constant. The R values obtained were $R_1 = 0.031$ and $R_2 = 0.046$.

At this point the location which had been assigned to the uncoordinated nitrogen atom of the pyrazole ligand was questioned. The root-mean-square (rms) amplitudes of thermal vibration for the two atoms bonded to the coordinated nitrogen atom were 0.258 (6), 0.293(6), 0.306(6) for the atom refined as nitrogen and 0.128(8), 0.202(6), 0.249(6) for the atom refined as carbon. The bond distances around the pyrazole ring were: (Mo)N-N(H), 1.339(5) Å; (H)N-C, 1.383(7) Å; C-C, 1.358(8) Å; C-C, 1.313(6) Å; and C-N(Mo), 1.338(5) Å. These values suggested that the identities of the atoms in question had been reversed. After the required switch in scattering factors, two additional cycles of refinement converged to $R_1 = 0.027$ and $R_2 = 0.037$. This resulted in rms values of 0.197(5), 0.245(4), 0.283(4) for

Table I. The Root-Mean-Square Amplitudes of Thermal Vibration.

Atom	Min.	Intermed.	Max.
Mo	0.1777(6)	0.1865(5)	0.2087(5)
1N(1)	0.184(4)	0.194(4)	0.220(4)
1N(2)	0.180(5)	0.193(4)	0.237(4)
1C(1)	0.191(6)	0.226(5)	0.305(5)
1C(2)	0.188(6)	0.244(5)	0.319(6)
1C(3)	0.188(6)	0.235(5)	0.252(5)
2N(1)	0.187(5)	0.206(4)	0.217(4)
2N(2)	0.193(4)	0.195(4)	0.210(4)
2C(1)	0.188(6)	0.220(5)	0.256(5)
2C(2)	0.184(6)	0.247(5)	0.285(5)
2C(3)	0.188(6)	0.229(5)	0.260(5)
3N(1)	0.192(4)	0.209(4)	0.220(4)
3N(2)	0.197(5)	0.245(4)	0.283(4)
3C(1)	0.176(7)	0.274(6)	0.333(6)
3C(2)	0.181(6)	0.264(6)	0.340(6)
3C(3)	0.199(6)	0.248(5)	0.264(5)
B	0.180(6)	0.199(6)	0.237(5)
C(4)	0.202(5)	0.238(5)	0.272(5)
C(5)	0.219(6)	0.279(6)	0.341(6)
C(6)	0.194(5)	0.228(5)	0.294(5)
C(7)	0.209(6)	0.262(6)	0.341(6)
C(8)	0.180(6)	0.276(5)	0.296(6)
C(9)	0.170(6)	0.238(5)	0.286(5)
C(10)	0.194(6)	0.253(5)	0.286(5)
C(11)	0.183(6)	0.224(5)	0.244(5)
C(12)	0.206(5)	0.216(6)	0.272(5)
O(1)	0.198(4)	0.265(4)	0.318(4)
O(2)	0.188(5)	0.270(4)	0.382(4)

(8) F.A. Cotton, B.A. Frenz, G. Deganello, and A. Shaver, *J. Organometal. Chem.*, *50*, 227 (1973).

(9) The following computer programs were used: DATARED by Frenz for data reduction; JIMDAP, a version of Zalkin's Fourier program FORDAP, as modified by Ibers; NUCLS, a full-matrix least-squares program by Ibers and Doedens, based on Busing and Levy's ORFLS program; RSCAN by Doedens for analysis of structure factors; ORTEP by Johnson for illustrations; ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson and Thiessen for distances and angles; LIST by Snyder for listing structure factors for publication.

(10) D.T. Cromer and J.T. Waber, «International Tables for X-ray Crystallography», Vol. IV, Kynoch Press, Birmingham, England, in press.

(11) D.T. Cromer and D. Liberman, *J. Chem. Phys.*, *53*, 1891 (1970).

Table II. Values of $10|F_o|$ and $10|F_c|$ (in Electrons).

Table III. Positional and Anisotropic Temperature Parameters for Non-Hydrogen Atoms[a].

Atom	x	y	z	β_{11} [b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.23192(3)	0.22190(2)	0.04461(1)	116.6(6)	36.7(2)	19.7(2)	8.3(2)	0.8(2)	—2.0(1)
1N(1)	0.3373(3)	0.3226(2)	0.1287(1)	106(5)	45(2)	23(1)	—7(2)	4(2)	—4(1)
1N(2)	0.2979(3)	0.3344(2)	0.1979(1)	121(5)	48(2)	22(1)	—14(3)	6(2)	—7(1)
1C(1)	0.3716(5)	0.4147(3)	0.2238(2)	191(8)	63(3)	32(1)	—36(4)	17(3)	—15(2)
1C(2)	0.4580(5)	0.4571(3)	0.1720(2)	210(8)	56(3)	41(2)	—44(4)	22(3)	—13(2)
1C(3)	0.4333(4)	0.3978(3)	0.1139(2)	138(6)	54(2)	31(1)	—20(3)	13(2)	0(1)
2N(1)	0.0800(3)	0.1689(2)	0.1320(1)	130(5)	39(2)	24(1)	—9(2)	1(2)	0(1)
2N(2)	0.0668(3)	0.2066(2)	0.1986(1)	115(5)	43(2)	22(1)	—3(2)	1(2)	2(1)
2C(1)	—0.0726(4)	0.1743(3)	0.2251(2)	118(6)	59(2)	30(1)	—6(3)	10(2)	8(2)
2C(2)	—0.1520(4)	0.1150(3)	0.1759(2)	132(6)	64(3)	38(1)	—31(4)	—4(3)	5(2)
2C(3)	—0.0537(4)	0.1137(3)	0.1186(2)	151(7)	47(2)	33(1)	—18(3)	—9(2)	—1(1)
3N(1)	0.0301(3)	0.3319(2)	0.0406(1)	133(5)	42(2)	25(1)	8(2)	4(2)	2(1)
3N(2)	—0.0111(4)	0.3881(2)	0.0953(2)	174(6)	64(2)	33(1)	34(3)	8(2)	—4(1)
3C(1)	—0.1408(5)	0.4437(3)	0.0770(3)	170(8)	60(3)	58(2)	42(4)	30(3)	22(2)
3C(2)	—0.1867(5)	0.4240(3)	0.0082(3)	128(7)	82(3)	53(2)	31(4)	0(3)	20(2)
3C(3)	—0.0787(5)	0.3546(3)	—0.0123(2)	153(7)	65(3)	31(1)	16(4)	—6(2)	7(2)
B	0.2149(5)	0.2533(3)	0.2452(2)	127(7)	55(3)	18(1)	—12(3)	1(2)	0(1)
C(4)	0.3444(5)	0.1695(3)	0.2674(2)	165(7)	74(3)	24(1)	—3(4)	—3(2)	5(2)
C(5)	0.5183(5)	0.2010(4)	0.2872(3)	154(8)	118(4)	42(2)	13(4)	—6(3)	5(2)
C(6)	0.1425(5)	0.3072(3)	0.3135(2)	162(7)	81(3)	25(1)	—19(4)	16(2)	—8(2)
C(7)	0.0130(6)	0.3866(3)	0.3011(3)	226(9)	70(3)	50(2)	—5(4)	39(3)	—19(2)
C(8)	0.3154(5)	0.0600(3)	0.0426(2)	226(9)	46(2)	42(2)	39(4)	1(3)	5(2)
C(9)	0.4331(5)	0.1205(3)	0.0752(2)	163(7)	58(2)	32(1)	46(4)	0(3)	2(2)
C(10)	0.5105(5)	0.1872(3)	0.0312(2)	140(7)	75(3)	36(1)	31(4)	7(3)	0(2)
C(11)	0.3154(5)	0.2909(3)	—0.0366(2)	136(6)	50(2)	28(1)	19(3)	7(2)	—5(2)
C(12)	0.1090(5)	0.1530(3)	—0.0319(2)	196(8)	48(2)	28(1)	10(3)	—11(3)	0(1)
O(1)	0.3592(4)	0.3333(2)	—0.0849(2)	239(6)	82(2)	30(1)	17(3)	30(2)	13(1)
O(2)	0.0371(4)	0.1137(2)	—0.0783(2)	358(8)	66(2)	36(1)	—3(3)	—47(2)	—13(1)

[a] The numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits. [b] The anisotropic temperature factor is in the form of $\exp[-10^4(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Table IV. Interatomic Distances(Å).

Atoms	Distance	Atoms	Distance
Mo-1N(1)	2.238(3)	B-1N(2)	1.607(5)
Mo-2N(1)	2.239(3)	B-2N(2)	1.585(5)
Mo-3N(1)	2.237(3)		
		B-C(4)	1.605(6)
Mo-C(8)	2.341(4)	B-C(6)	1.625(6)
Mo-C(9)	2.206(3)		
Mo-C(10)	2.347(4)	C(4)-C(5)	1.506(6)
		C(6)-C(7)	1.531(6)
Mo-C(11)	1.956(4)		
Mo-C(12)	1.950(4)	C(8)-C(9)	1.387(6)
		C(9)-C(10)	1.412(6)
C(11)-O(1)	1.156(4)	C(8)-C(10)	2.389(7)
C(12)-O(2)	1.156(4)		

Pyrazolyl and pyrazole rings[a]

Atoms	Ring 1	Ring 2	Ring 3
N(1)-N(2)	1.367(4)	1.367(4)	1.348(4)
N(2)-C(1)	1.340(4)	1.343(4)	1.334(5)
C(1)-C(2)	1.368(5)	1.368(5)	1.353(6)
C(2)-C(3)	1.371(5)	1.380(5)	1.373(6)
C(3)-N(1)	1.341(4)	1.341(4)	1.330(4)

[a] Ring 1, ring 2, and ring 3 are identified in Figure 1 by the numbers prefixed to the atom labels.

Table V. Bond Angles (Deg).

Atoms	Ring 1	Ring 2	Ring 3
N(1)-Mo-C(8)	120.5(1)	82.7(1)	149.7(1)
N(1)-Mo-C(9)	88.0(1)	92.0(1)	166.7(1)
N(1)-Mo-C(10)	82.6(1)	126.3(1)	148.0(1)
N(1)-Mo-C(11)	96.4(1)	164.9(1)	86.1(1)
N(1)-Mo-C(12)	169.2(1)	95.6(1)	88.0(1)
N(1)-N(2)-C(1)	108.7(3)	109.1(3)	111.5(3)
N(2)-C(1)-C(2)	109.5(3)	108.9(3)	107.3(4)
C(1)-C(2)-C(3)	104.7(3)	105.2(3)	105.4(4)
C(2)-C(3)-N(1)	111.0(3)	110.4(3)	111.4(3)
C(3)-N(1)-N(2)	106.2(3)	106.3(3)	104.4(3)
Mo-N(1)-N(2)	130.1(2)	128.6(2)	125.7(2)
Mo-N(1)-C(3)	122.6(2)	121.9(2)	129.8(3)
B-N(2)-N(1)	125.0(3)	124.2(3)	—
B-N(2)-C(1)	124.8(3)	124.2(3)	—
N(2)-B-C(4)	110.9(3)	108.4(3)	—
N(2)-B-C(6)	107.6(3)	108.8(3)	—

Atoms	Angle	Atoms	Angle
1N(1)-Mo-2N(1)	83.7(1)	Mo-C(8)-C(9)	67.0(2)
1N(1)-Mo-3N(1)	81.3(1)	Mo-C(9)-C(8)	77.6(2)
2N(1)-Mo-3N(1)	79.0(1)	Mo-C(9)-C(10)	77.4(2)
C(8)-Mo-C(9)	35.4(1)	Mo-C(10)-C(9)	66.6(2)
C(8)-Mo-C(10)	61.3(2)	Mo-C(11)-O(1)	177.5(3)
C(8)-Mo-C(11)	109.8(1)	Mo-C(12)-O(2)	178.4(4)
C(8)-Mo-C(12)	69.9(2)		
C(9)-Mo-C(10)	36.0(1)	B-C(4)-C(5)	116.7(4)
C(9)-Mo-C(11)	103.0(2)	B-C(6)-C(7)	119.2(3)
C(9)-Mo-C(12)	102.8(2)		
C(10)-Mo-C(11)	68.4(2)	1N(2)-B-2N(2)	108.0(3)
C(10)-Mo-C(12)	106.1(2)	C(4)-B-C(6)	113.0(3)
C(11)-Mo-C(12)	81.4(2)	C(8)-C(9)-C(10)	117.2(4)

the atom refined as nitrogen and 0.199(6), 0.248(5), 0.264(5) for the atom refined as carbon, as given in Table I. The bond distances in the pyrazole ring were then consistent with previously reported values, *vide infra*.

In the last cycle of least-squares refinement the largest parameter shift was less than 0.80 times its estimated standard deviation. The error in an observation of unit weight was 1.22. No unusual trends were found in a comparison of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|, \lambda^{-1}\sin\theta$, reflection number, or classes of Miller indices. A final difference Fourier was featureless with the highest peak at 0.42(5)e Å^{-3}. A list of observed and calculated structure factors (F_{000} = 238) is given in Table II.

Table VI. Weighted Least-squares Planes[a] and Related Parameters.

1. Planes through Pyrazolylborate and Pyrazole Rings:

Equation of Planes[b]
Ring 1: $6.434x-7.354y+4.823z-0.4149 = 0$
Ring 2: $3.836x-10.896y+6.908z+0.6227 = 0$
Ring 3: $5.145x+9.902y-6.305z-3.185 = 0$

Deviations (Å) of Atoms from Plane:

	N(1)	N(2)	C(1)	C(2)	C(3)
Ring 1:	0.003(3)	−0.004(3)	0.005(4)	0.000(5)	−0.004(4)
Ring 2:	0.001(3)	−0.001(3)	0.000(4)	0.002(4)	−0.003(4)
Ring 3:	0.000(3)	0.000(4)	−0.001(5)	0.002(5)	−0.001(4)

2. Mo Coordination Plane (1N(1), 2N(1). C(11), C(12)):

Equation of Plane: $5.861x-9.456y+1.464z+0.9088=0$

Deviations (Å) of Atoms from Plane

1N(1)	0.023(3)	C(11)	−0.047(4)
2N(1)	−0.026(3)	C(12)	0.054(4)

Distance of Mo from Plane: 0.235 Å

3. «Mirror» Plane (Mo, B, C(9), 3N(1), C(4), C(6))

Equation of the plane[c]: $5.617x+10.014y-1.028-3.479=0$

Deviations (Å) of Atoms from Plane:

Mo	0.0001(3)	C(4)	−0.121(4)	C(9)	0.084(4)
B	0.013(4)	C(6)	0.076(4)	3N(1)	−0.028(3)

Distances (Å) of the Remaining Atoms from the Plane:

	N(1)	N(2)	C(1)	C(2)	C(3)
Ring 1:	1.514	1.340	2.531	3.494	2.822
Ring 2:	−1.474	−1.239	−2.372	−3.362	−2.764
Ring 3:		0.247	0.095	−0.290	−0.358

C(5)	1.150	C(8)	−1.150	C(11)	1.244
C(7)	0.156	C(10)	1.231	C(12)	−1.302
O(1)	1.964	O(2)	−2.051		

4. BN_4Mo Chelate Ring

Equation I: (B, 1N(2), 2N(2)) $-5.231x+9.500y+7.105z-3.025 = 0$

Equation II: (1N(1), 2N(1), 1N(2), 2N(2)) $5.403x-9.261y+5.508z+0.4310 = 0$

Equation III: (Mo, 1N(1), 2N(1)) $5.624z-9.323y+4.121z+0.5806 = 0.$

Deviations of Atoms from Plane II Å

1N(1)	−0.026(3)	1N(2)	0.033(3)
2N(1)	0.026(3)	2N(2)	−0.028(3)

Mo −0.125 B 0.597

Dihedral Angles, (Degrees)

Φ (I, II) 140.6 Φ (II, III) 4.4

[a] The equation of the plane has the form $Ax+By+Cz-D = 0$, where x, y, and z are fractional monoclinic coordinates. [b] The dihedral angle between mean planes through rings 1 and 2 is 24.2°. [c] The dihedral angle between this plane and the mean plane through ring 3 is 16.7°.

Results

X-ray crystallographic analysis of the yellow tabular crystal showed it to be the pyrazole adduct of [diethylbis(1-pyrazole)borato](η^3-allyl)-dicarbonylmolybdenum, *viz.*, $[Et_2B(pz)_2](\eta^3\text{-}C_3H_5)(Hpz)(CO)_2Mo$. This compound has been described previously[7]. We showed that the addition of pyrazole to the original sample transformed it entirely into a compound whose ir and nmr spectra agreed with that originally reported.[7]

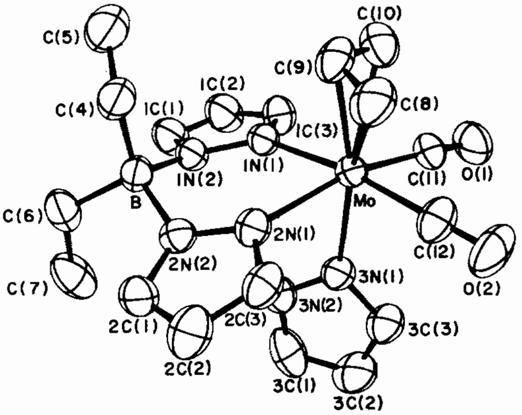

Figure 1. View of the molecular structure of $[Et_2B(pz)_2]$-(η^3-C_3H_5)(Hpz)$(CO)_2Mo$ showing the 50% probability ellipsoids and the atomic numbering scheme.

The molecular structure with the crystallographic numbering scheme is shown in Figure 1. The fractional coordinates and anisotropic thermal parameters with their estimated standard deviations are given for the non-hydrogen atoms in Table III. Interatomic distances and angles are listed in Tables IV and V, respectively. Table VI gives various least-squares planes and associated parameters.

Discussion

Molecules of $[Et_2B(pz)_2](\eta^3C_3H_5)(Hpz)(CO)_2Mo$ are well-separated in the unit cell, with the shortest intermolecular contact being 3.241(5) Å.

The molecule has an approximate mirror plane of symmetry passing through the Mo and B atoms and the center atom, C(9), of the allyl group. Only the methyl carbon atoms, C(5) and C(7), appreciably violate this symmetry. Considering the allyl group as a unidentate ligand, the coordination about the Mo atom is octahedral with CO groups trans to the pyrazolylborate N atoms and the allyl group trans to the N atom of the pyrazole ring. The uncoordinated N atom of the pyrazole group lies on the pyrazolylborate side of the molecule; the arc formed by the allyl carbon atoms opens toward the carbonyl side of the molecule.

Table VII. Metal-Boron Non-bonded Contacts in Metal Pyrazolylborate Complexes

Compound	Mean M - - - B Distance (Å)	Comments
$[H_2B(Me_2pz)_2](\eta^3\text{-}C_7H_7)(CO)_2Mo$	2.797(5)	bidentate, see ref. 5
$[H_2B(Me_2pz)_2](\eta^3\text{-}C_3H_5)(CO)_2Mo$	2.81	bidentate, see ref. 6
$[HB(pz)_3](COCH_3)(CO)_2Fe$	3.147(5)	tridentate, see ref. 18
$[HB(pz)_3]_2Co$	3.195(4)	tridentate, see ref. 19
$[HB(pz)_3](N_2C_6H_5)(CO)_2Mo$	3.345	tridentate, see ref. 20
$[B(pz)_4](\eta^5\text{-}C_5H_5)(CO)_2Mo$	3.73	bidentate, see ref. 17
$[Et_2B(pz)_2](\eta^3\text{-}C_3H_5)(Hpz)(CO)_2Mo$	3.806(4)	bidentate, this work

Except for the conformation of the MoNNBNN ring, *vide infra,* the molecule presents no unusual or unexpected features and compares well with previous structures. Because the structural work on polypyrazolylborate complexes has recently been reviewed,[12] we will not discuss it in detail here. As shown in Tables IV and V, there is no essential difference between pyrazolyl and pyrazole rings with respect to bond distances and angles. Only the N-N distance is significantly different in the two rings; the distance is 1.367(4) Å in both pyrazolyl rings and is 0.019 Å longer than the N-N distance of 1.348 (4) Å in the pyrazole ring. The average of five N-N distances determined in $Ni(Hpz)_4Cl_2$,[13] $Ni(Hpz)_4Br_2$,[14] and $Ni(Hpz)_6(NO_3)_2$[15] is 1.346 Å and, as we find here, this distance is shorter than the mean of 1.364 (3) Å found for six pyrazolylborate structures.[12] In uncoordinated pyrazole the distance is 1.342(2).[16]

Bond distances in both pyrazolyl rings and pyrazole rings follow a characteristic pattern: the longest bond is the C-C bond opposite the N coordinated to B or H, the other C-C bond is slightly shorter (by *ca.* 0.01 Å), and the C-N bonds are similar in length but *ca.* 0.03-0.04 Å shorter than the C-C bonds. The narrow range of distances (1.33 to 1.38 Å) in each ring suggests a fair amount of electron delocalization and points out the naiveté of representing the ring with localized single and double bonds.

In all previous structural determinations of metal pyrazolylborate complexes,[5,6,12,17-20] the MNNBNN unit is in a boat conformation. This is obviously to be expected in the case of tridentate pyrazolylborates. For the bidentate pyrazolylborates the boat conformation also seems logical since only in this case (or for a planar six-membered ring) can the sp^2-hybridized N atoms be in planar environments. In the present structure the MoNNBNN ring assumes a distorted chair conformation. The Mo and B atoms are displaced from the mean plane through the four N atoms by −0.125 and +0.597 Å, respectively (see Table VI). The dihedral angle between the N_4 plane and the MoN_2 plane is 4.4°, while that between the N_4 plane and the BN_2 plane is 140.6°.

The inability of the present compound to assume a boat conformation for the MoNNBNN moiety is probably the result of the short intramolecular contact between the H atom on C(9) of the allyl group and one of the H atoms on C(4) of an ethyl group. This distance of 2.2 Å would be reduced in the boat conformation. The formation of the boat in the alternative sense, *i.e.*, such that the boat opened toward the pyrazole ligand, would be blocked by a short contact between the H atom on 3N(2) and an H atom on C(6).

It is noteworthy that from ir and pmr studies[17] of $[B(pz)_4](\eta^5\text{-}C_5H_5)(CO)_2Mo$ it has been shown that the two boat conformers interconvert in solution. The ir spectrum of the present compound does not show the characteristic splitting of the CO stretching bands (by *ca.* 15-20 cm^{-1}) observed in the previous work. This is in agreement with the statement that the molecule cannot isomerize, owing to significant non-bonded contacts.

An additional structural feature is noted in a tabulation of M . . . B distances as given in Table VII. The first two compounds listed involve electron-deficient metal atoms that apparently form 3-center, 2-electron M-H-B bonds to overcome his deficiency. Thus the M · · · B distances are short and in the range 2.8 to 3.0 Å. The next three compounds have tridentate pyrazolylborate ligands; thus the M · · · B distance is essentially fixed and varies only with metallic radius. In the last two compounds the metal atoms have a satisfactory eighteen-electron configuration; hence there is no need for a close contact between the Mo atom and an H atom on boron.. The Mo · · · B distance is correspondingly long at 3.7 to 3.8 Å.

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