A Bispyrazolylboratoallyldicarbonylmolybdenum Complex with a 16-Electron Configuration

F. Albert Cotton,* Bertram A. Frenz, and Carlos A. Murillo

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received August 21, 1974*

Abstract: The structure of (diphenyldipyrazolyborato)(2-methylallyl)dicarbonylmolybdenum has been determined by X-ray crystallography. The molybdenum atom is coordinated by the η^3-allyl ligand, two CO ligands, and the nitrogen atoms of the two pyrazole rings. In contrast to the analogous compounds in which the dipyrazolyl ligand is $H_2B(pz)_2$ and $(C_2H_5)_2B(pz)_2$ (pz = 1-pyrazolyl) where the dipyrazolylborate ligand interacts further with the molybdenum atom, through one of the B–H groups or through a methylene C–H bond, there is no further ligation of the molybdenum atom. It is thus left with a 16-electron valence shell configuration. Interaction with an ortho C–H bond of one of the phenyl groups does not occur as might have been expected. The reason for this appears to be that the orientation of one phenyl group which would be required for such an interaction is inconsistent with the attainment of a satisfactory conformation of the entire set of rings ($2C_6H_5$ and $2C_3N_2H_3$) about the boron atom. Given the fixed orientation of the two pyrazole rings, owing to their participation in the dipyrazolylboratomolybdenum chelate ring, the only acceptable conformation of the phenyl rings is one in which the phenyl ring that might have been able to provide an ortho C–H ···Mo interaction is forced into a rotational orientation approximately perpendicular to that which would allow a C–H ··· Mo interaction. Another surprising structural feature of this molecule is the occurrence of very small C–C–C angles (ca. 114°) at the two phenyl carbon atoms bonded to the boron atom. The compound crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 8.837$ (4) Å, $b = 10.785$ (3) Å, $c = 24.170$ (3) Å, $\beta = 97.93$ (2)°, $V = 2281$ (1) Å^3, and $Z = 4$. The structure was solved and refined using 1677 reflections for which $I > 3\sigma(I)$ collected with Mo Kα radiation by the $\theta/2\theta$ scan technique on a Syntex P1 diffractometer. Final discrepancy indices were $R_1 = 5.2\%$ and $R_2 = 7.1\%$. Other than the small C–C–C angles already mentioned, no unusual bond distances or angles were observed.

The general class of compounds $(R_2B(pz)_2)(CO)_2$(enyl)Mo, first prepared by Trofimenko,[1] has been shown by subsequent structural studies to exhibit a variety of unexpected but significant, and often unique, structural and dynamical characteristics. When the enyl ligand is a 5-electron donor dienyl, namely η^5-C_5H_5, there is clearly an 18-electron configuration in the valence orbitals of the molybdenum atom,[2] and the number and types of metal to ligand bonds are conventional, predictable, and in accord with the structure found (for R = pz) crystallographically.[3] This molecule was not without interest; however, since it was shown[3] by NMR to be conformationally labile, with the dipyrazolylboratomolybdenum ring fluctuating between the two boat conformations in which B and Mo occupy bow and stern positions. This sort of conformational lability has been found to be characteristic of all such rings and allowance must be made for it in the interpretation of the NMR spectra of all other, more complex, dipyrazolylboratomolybdenum compounds.

In cases where the enyl ligand is an allyl group, i.e., a three-electron donor, the seemingly obvious way of counting electrons would lead to the conclusion that the molybdenum atoms in such compounds have 16-electron valence shell configurations. However, in several cases where we have carried out crystallographic and/or NMR investigations, this has not actually been the case because of additional but unanticipated interactions of the dipyrazolylborato ligands with the molybdenum atom.

The first such investigations[4,5] dealt with $[H_2B(3,5\text{-dimethylpyrazolato})_2](CO)_2(C_7H_7)Mo$, and it was shown that the C_7H_7 ring is η^3. However, the dipyrazolylboratomolybdenum six-ring is severely puckered so that the boron to molybdenum distance is only about 2.80 Å. This severely puckered conformation is stabilized by an interaction of one of the hydrogen atoms bonded to boron with the molybdenum atom, so that the H ··· Mo distance is only ca. 2.10 Å. It was proposed that the B–H ··· Mo group could be treated as a case of three-center, two electron (3c-2e) bonding and that because of its partial share in this electron pair the molybdenum atom effectively achieves an 18-electron configuration.

We next examined[6,7] the diethyl compound $[(C_2H_5)_2B(pz)_2](CO)_2$(2-phenylallyl)Mo and found that a similar but even more surprising device for the avoidance of a 16-electron configuration was employed. In this case, an α hydrogen atom of one ethyl group is involved in a strong interaction with the molybdenum atom (H ··· Mo, ca. 2.15 Å) and the C–H ··· Mo group can be viewed as containing a 3c-2e bond. Again, because of its share in such a 3c-2e system, the molybdenum atom effectively achieves an 18-electron configuration. It has also been shown that the C–H ··· Mo interaction is sufficiently strong to remain intact even when the enyl ligand is C_7H_7 which could increase its hapticity from 3 to 5.[8]

Thus it began to appear that none of the "16-electron complexes" originally discussed by Trofimenko would actually warrant this description. However, we now report one genuine 16-electron system, describe its structure in detail, and provide an explanation for its failure to avoid having such an incomplete valence shell configuration. The compound in question is $[(C_6H_5)_2B(pz)_2](CO)_2$(2-methylallyl)Mo.

Experimental Section

A sample of the compound was kindly supplied by Dr. S. Trofimenko. The material was first purified by chromatography on neutral alumina using dichloromethane solvent and crystallized from dichloromethane to obtain crystals suitable for structure analysis.

Data Collection. A crystal measuring about 0.11 × 0.15 × 0.48 mm was mounted in a sealed capillary and examined on a Syntex P$\bar{1}$ four-circle, automatic diffractometer. From ω scans of several intense reflections and axial photographs, the quality of the crystal was confirmed and the mosaicity was seen to be satisfactory. A peak width at half-height of 0.2° was found.

Data were collected at 23° ± 2° using graphite-monochromatized Mo Kα radiation and a θ–2θ scan rate varying from 4 to 24°/min, depending on the intensity of the reflection. Of the 2671 reflections collected in the range $0° < 2\theta(\text{Mo K}\alpha) \leq 42°$, 1677 unique observations with $I > 3\sigma(I)$ were retained as observed data. Three standard reflections measured repeatedly every 100 data points were stable and showed no significant time dependence. The

Table I. Positional and Temperature Parameters[a,b] for $[Ph_2B(pz)_2][\eta^3\text{-}CH_2CH(CH_3)CH_2](CO)_2Mo$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	−0.0327 (1)	0.22331 (9)	0.16155 (4)	122 (1)	84 (1)	11.5 (2)	5 (1)	3.7 (4)	3.7 (4)
1N(1)	−0.1045 (13)	0.4132 (9)	0.1393 (3)	188 (22)	88 (11)	9 (1)	5 (14)	6 (5)	−3 (3)
2N(1)	0.1647 (10)	0.3286 (9)	0.2088 (4)	107 (15)	74 (10)	17 (2)	17 (10)	10 (5)	3 (3)
1N(2)	−0.0037 (10)	0.4943 (9)	0.1209 (3)	104 (15)	89 (12)	11 (1)	3 (12)	15 (4)	2 (3)
2N(2)	0.2321 (11)	0.4191 (9)	0.1810 (3)	120 (17)	94 (12)	11 (2)	−5 (11)	−11 (5)	−2 (4)
1C(1)	−0.0821 (20)	0.6001 (12)	0.1062 (5)	312 (36)	59 (14)	14 (2)	25 (19)	−4 (8)	6 (4)
1C(2)	−0.2328 (15)	0.5865 (13)	0.1132 (5)	107 (23)	106 (18)	20 (3)	33 (15)	−2 (6)	5 (5)
1C(3)	−0.2454 (14)	0.4686 (14)	0.1334 (5)	104 (22)	120 (19)	17 (3)	8 (16)	0 (6)	−7 (6)
2C(1)	0.3487 (14)	0.4653 (13)	0.2154 (5)	127 (21)	131 (19)	15 (3)	29 (16)	3 (7)	6 (6)
2C(2)	0.3580 (14)	0.4098 (13)	0.2664 (5)	116 (22)	150 (18)	16 (3)	−8 (16)	−9 (6)	5 (6)
2C(3)	0.2388 (15)	0.3265 (13)	0.2612 (5)	159 (23)	128 (16)	10 (2)	15 (16)	−3 (6)	8 (5)
B	0.1639 (15)	0.4484 (12)	0.1187 (5)	128 (24)	80 (16)	12 (3)	−13 (16)	2 (6)	−1 (5)
C(4)	0.2555 (13)	0.5567 (11)	0.0930 (5)	118 (19)	83 (14)	13 (2)	19 (13)	0 (6)	2 (4)
C(5)	0.3127 (13)	0.5455 (11)	0.0407 (5)	99 (19)	95 (15)	16 (3)	−9 (13)	10 (6)	−4 (5)
C(6)	0.3791 (14)	0.6416 (13)	0.0172 (5)	146 (22)	114 (18)	17 (3)	−17 (17)	19 (6)	4 (6)
C(7)	0.4030 (14)	0.7535 (12)	0.0438 (6)	151 (22)	93 (18)	25 (3)	−11 (14)	0 (7)	14 (6)
C(8)	0.3562 (16)	0.7682 (13)	0.0947 (5)	206 (25)	103 (16)	15 (3)	−13 (17)	8 (7)	−4 (6)
C(9)	0.2828 (16)	0.6739 (13)	0.1182 (5)	243 (27)	120 (17)	9 (2)	−18 (18)	13 (6)	−4 (5)
C(10)	0.1521 (13)	0.3204 (11)	0.0847 (4)	99 (18)	90 (14)	12 (2)	29 (13)	13 (6)	5 (4)
C(11)	0.0272 (14)	0.2860 (12)	0.0447 (4)	159 (21)	86 (13)	12 (2)	−5 (15)	8 (6)	4 (5)
C(12)	0.0373 (16)	0.1870 (13)	0.0083 (5)	185 (27)	112 (17)	11 (2)	−24 (17)	2 (6)	−2 (5)
C(13)	0.1681 (19)	0.1184 (12)	0.0109 (5)	256 (31)	85 (15)	15 (3)	−22 (19)	29 (8)	−9 (5)
C(14)	0.2943 (15)	0.1463 (12)	0.0497 (5)	177 (25)	93 (16)	18 (3)	−3 (16)	21 (8)	−3 (5)
C(15)	0.2838 (14)	0.2445 (11)	0.0857 (5)	151 (22)	87 (15)	14 (2)	−5 (15)	−2 (6)	2 (5)
C(16)	0.0123 (12)	0.0185 (12)	0.1376 (5)	81 (18)	112 (15)	19 (3)	−7 (13)	11 (6)	1 (5)
C(17)	0.1023 (13)	0.0493 (11)	0.1894 (5)	66 (19)	107 (15)	22 (3)	34 (14)	0 (7)	9 (5)
C(18)	0.0185 (16)	0.0735 (13)	0.2331 (5)	241 (28)	116 (16)	15 (3)	44 (17)	16 (8)	9 (5)
C(19)	0.2730 (17)	0.0481 (13)	0.1976 (5)	242 (31)	107 (17)	20 (3)	25 (17)	12 (8)	7 (5)
C(20)	−0.2070 (18)	0.1570 (13)	0.1171 (5)	184 (26)	116 (17)	17 (3)	70 (19)	9 (7)	10 (6)
C(21)	−0.1760 (14)	0.2319 (12)	0.2126 (5)	125 (20)	100 (15)	20 (3)	9 (15)	8 (6)	11 (5)
O(1)	−0.3254 (12)	0.1188 (10)	0.0918 (4)	183 (18)	174 (15)	29 (3)	5 (13)	−13 (6)	3 (5)
O(2)	−0.2732 (12)	0.2416 (9)	0.2418 (4)	234 (19)	137 (13)	31 (2)	24 (12)	45 (6)	14 (4)
H(5)	0.3037	0.4682	0.0218						
H(6)	0.4098	0.6307	−0.0186						
H(7)	0.4510	0.8195	0.0268						
H(8)	0.3750	0.8445	0.1141						
H(9)	0.2481	0.6885	0.1532						
H(11)	−0.0657	0.3316	0.0425						
H(12)	−0.0477	0.1668	−0.0186						
H(13)	0.1733	0.0508	−0.0141						
H(14)	0.3854	0.0987	0.0517						
H(15)	0.3698	0.2624	0.1127						
1H(1)	−0.0392	0.6730	0.0927						
1H(2)	−0.3122	0.6468	0.1058						
1H(3)	−0.3367	0.4315	0.1418						
2H(1)	0.4141	0.5307	0.2063						
2H(2)	0.4313	0.4248	0.2985						
2H(3)	0.2128	0.2747	0.2904						
H(16-A)	−0.0959	0.0155	0.1350						
H(16-B)	0.0596	0.0003	0.1053						
H(18-A)	0.0692	0.0947	0.2695						
H(18-B)	−0.0897	0.0683	0.2269						
H(19-A)	0.3209	0.0734	0.1650						
H(19-B)	0.3061	−0.0336	0.2077						
H(19-C)	0.3075	0.1033	0.2275						

[a] All values for the temperature factors have been multiplied by 10^4. Temperature factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The isotropic temperature factor for all hydrogens was fixed at 5.0 Å^2.

linear absorption coefficient of the compound is 6.05 cm^{-1} and no absorption correction was applied.

To calculate the lattice parameters, setting angles for 15 of the strongest reflections in the range $18° < 2\theta < 34°$ were carefully measured. A least-squares refinement gave a = 8.837 (4) Å, b = 10.785 (3) Å, c = 24.170 (3) Å, β = 97.93 (2)°, and V = 2281 (1) Å^3. The systematic absences uniquely indicated the monoclinic space group $P2_1/c$. With Z = 4 and a molecular weight of 506.20 g mol^{-1}, the calculated density is 1.472 g cm^{-3}.

Solution and Refinement of the Structure.[9] The position of the molybdenum atom was obtained from a three-dimensional Patterson function. A least-squares cycle and a difference Fourier revealed all the rest of the nonhydrogen atoms. Another cycle of full-matrix least-squares refinement varying the atomic positional parameters using isotropic temperature factors resulted in discrepancy indices of

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.080$$

and

$$R_2 = [\Sigma w(|F_o - F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.103$$

Refinement was continued with isotropic and later anisotropic thermal parameters until the structure converged with final R factors of 0.063 and 0.083.

An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ showed that the original choice (0.06) for the p parameter used in the calculation of the standard deviation of the intensity (cf. the program DATARED[9]) was too small. The value 0.07 was indicated to be more suitable choice and it was used in the final cycles of refinement. At this point, the positions of the hydrogen atoms were also calculated and two more cycles of least-squares refinement were done in which the hydrogen positions were not varied. This gave final R_1 =

Table II. Root-Mean-Square Amplitudes of Thermal Vibration (Å)

Atom	Min	Intermed	Max
Mo	0.179 (2)	0.217 (2)	0.228 (2)
1N(1)	0.17 (2)	0.23 (2)	0.27 (2)
2N(1)	0.18 (2)	0.21 (2)	0.24 (1)
1N(2)	0.15 (2)	0.21 (2)	0.23 (1)
2N(2)	0.15 (2)	0.24 (2)	0.25 (1)
1C(1)	0.17 (2)	0.22 (2)	0.36 (2)
1C(2)	0.17 (2)	0.25 (2)	0.27 (2)
1C(3)	0.19 (2)	0.22 (2)	0.28 (2)
2C(1)	0.20 (2)	0.23 (2)	0.29 (2)
2C(2)	0.18 (2)	0.25 (2)	0.30 (2)
2C(3)	0.16 (2)	0.26 (2)	0.28 (2)
B	0.19 (2)	0.21 (2)	0.24 (2)
C(4)	0.18 (2)	0.21 (2)	0.24 (2)
C(5)	0.19 (2)	0.21 (2)	0.24 (2)
C(6)	0.19 (2)	0.25 (2)	0.27 (2)
C(7)	0.21 (2)	0.24 (2)	0.30 (2)
C(8)	0.21 (2)	0.25 (2)	0.29 (2)
C(9)	0.16 (2)	0.26 (2)	0.31 (2)
C(10)	0.16 (2)	0.19 (2)	0.25 (2)
C(11)	0.18 (2)	0.23 (2)	0.25 (2)
C(12)	0.18 (2)	0.24 (2)	0.29 (2)
C(13)	0.18 (2)	0.22 (2)	0.33 (2)
C(14)	0.20 (2)	0.23 (2)	0.27 (2)
C(15)	0.20 (2)	0.23 (2)	0.25 (2)
C(16)	0.17 (2)	0.24 (2)	0.26 (2)
C(17)	0.14 (2)	0.25 (2)	0.28 (2)
C(18)	0.20 (2)	0.24 (2)	0.33 (2)
C(19)	0.22 (2)	0.26 (2)	0.31 (2)
C(20)	0.18 (2)	0.23 (2)	0.32 (2)
C(21)	0.21 (2)	0.22 (2)	0.27 (2)
O(1)	0.23 (1)	0.32 (1)	0.33 (1)
O(2)	0.22 (1)	0.27 (1)	0.36 (1)

Table III. Interatomic Distances (Å)$^{a-c}$

Atoms	Distance	Atoms	Distance
Mo–1N(1)	2.19 (1)	B–1N(2)	1.57 (1)
Mo–2N(1)	2.26 (1)	B–2N(2)	1.57 (1)
Mo–C(16)	2.33 (1)	B–C(4)	1.60 (2)
Mo–C(17)	2.28 (1)	B–C(10)	1.60 (2)
Mo–C(18)	2.36 (1)	C(16)–C(17)	1.43 (1)
Mo–C(20)	1.89 (1)	C(17)–C(18)	1.40 (1)
Mo–C(21)	1.89 (1)	C(17)–C(19)	1.49 (2)
Mo–C(10)	2.84 (1)	C(20)–O(1)	1.21 (2)
Mo–C(11)	3.02 (1)	C(21)–O(2)	1.19 (1)
Mo–B	3.24 (1)		
		Phenyl Rings	
C(4)–C(5)	1.43 (2)	C(10)–C(11)	1.41 (2)
C(5)–C(6)	1.35 (2)	C(11)–C(12)	1.39 (2)
C(6)–C(7)	1.37 (2)	C(12)–C(13)	1.37 (2)
C(7)–C(8)	1.36 (2)	C(13)–C(14)	1.39 (2)
C(8)–C(9)	1.37 (2)	C(14)–C(15)	1.38 (2)
C(9)–C(4)	1.41 (2)	C(15)–C(10)	1.42 (2)

	Pyrazolyl Rings	
Atoms	Ring 1	Ring 2
N(1)–N(2)	1.37 (1)	1.37 (1)
N(2)–C(1)	1.36 (2)	1.33 (1)
C(1)–C(2)	1.37 (2)	1.36 (2)
C(2)–C(3)	1.37 (2)	1.38 (2)
C(3)–N(1)	1.37 (1)	1.34 (1)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. [b] Atoms are labeled as in Figure 1. [c] Rings 1 and 2 are identified in Figure 1 by the numbers prefixed to the atom labels.

0.052 and R_2 = 0.071, with the error in observation of unit weight of 1.546.

No unusual trends were observed in an analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of reflection number, $\lambda^{-1} \sin \theta$, or various classes of indices. A table of observed and calculated structure factor amplitudes is available.[10]

Table IV. Bond Angles (deg)

Atoms	Pz ring 1	Pz ring 2
N(1)–Mo–C(20)	91.7 (5)	171.8 (4)
N(1)–Mo–C(21)	85.3 (5)	100.7 (4)
N(1)–Mo–C(16)	151.5 (4)	117.1 (4)
N(1)–Mo–C(17)	165.1 (4)	85.9 (4)
N(1)–Mo–C(18)	147.0 (4)	85.2 (4)
N(1)–N(2)–C(1)	107 (1)	108.2 (9)
N(2)–C(1)–C(2)	110 (1)	110 (1)
C(1)–C(2)–C(3)	106 (1)	105 (1)
C(2)–C(3)–N(1)	109 (1)	110 (1)
C(3)–N(1)–N(2)	108 (1)	107 (1)
Mo–N(1)–N(2)	120.2 (8)	118.1 (7)
Mo–N(1)–C(3)	131.5 (9)	135.2 (9)
B–N(2)–N(1)	118 (1)	118.6 (9)
B–N(2)–C(1)	135 (1)	133 (1)
N(2)–B–C(4)	108.3 (9)	111.9 (9)
N(2)–B–C(10)	107.1 (9)	107.9 (9)
1N(2)–B–2N(2)	105.6 (9)	
C(4)–B–C(10)	116 (1)	
B–C(4)–C(5)	123 (1)	
B–C(4)–C(9)	124 (1)	
B–C(10)–C(11)	124 (1)	
B–C(10)–C(15)	119 (1)	

Atoms	Angle	Atoms	Angle
C(4)–C(5)–C(6)	122 (1)	Mo–C(17)–C(18)	76.0 (7)
C(5)–C(6)–C(7)	122 (1)	Mo–C(18)–C(17)	69.1 (7)
C(6)–C(7)–C(8)	119 (1)	Mo–C(17)–C(19)	121.6 (9)
C(7)–C(8)–C(9)	121 (1)	Mo–C(20)–O(1)	175 (1)
C(8)–C(9)–C(4)	123 (1)	Mo–C(21)–O(2)	175 (1)
C(9)–C(4)–C(5)	113 (1)	C(20)–Mo–C(21)	79.8 (5)
C(10)–C(11)–C(12)	121 (1)	C(20)–Mo–C(16)	69.8 (5)
C(11)–C(12)–C(13)	121 (1)	C(20)–Mo–C(17)	102.0 (5)
C(12)–C(13)–C(14)	121 (1)	C(20)–Mo–C(18)	102.4 (5)
C(13)–C(14)–C(15)	118 (1)	C(21)–Mo–C(16)	111.2 (5)
C(14)–C(15)–C(10)	124 (1)	C(21)–Mo–C(17)	102.6 (5)
C(15)–C(10)–C(11)	115 (1)	C(21)–Mo–C(18)	68.5 (5)
C(16)–C(17)–C(18)	115 (1)	C(16)–Mo–C(17)	36.1 (4)
C(16)–C(17)–C(19)	123 (1)	C(17)–Mo–C(18)	34.9 (4)
C(18)–C(17)–C(19)	122 (1)	C(16)–Mo–C(18)	60.8 (4)
Mo–C(16)–C(17)	69.9 (7)	1N(1)–Mo–2N(1)	80.3 (4)
Mo–C(17)–C(16)	74.1 (6)		

Table V. Unweighted Least-Squares Planes^a

1. Pyrazolylborate Rings

Plane I (Ring 1): $0.72x + 3.75y + 21.87z - 4.51 = 0$

Plane II (Ring 2): $-5.81x + 7.48y + 9.15z - 3.43 = 0$

Deviations of Atoms from Plane

	N(1)	N(2)	C(1)	C(2)	C(3)
Ring 1	0.01	−0.01	0.01	0.00	−0.01
Ring 2	−0.02	0.01	0.00	−0.01	0.01

2. Phenyl Rings

Plane III: $7.33x - 3.43y + 8.14z - 0.73 = 0$

Deviations of Atoms from Plane

C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
−0.01	0.02	−0.01	−0.01	0.01	−0.01

Plane IV: $-3.81x - 6.61y + 17.14z + 1.23 = 0$

Deviations of Atoms from Plane

C(10)	C(11)	C(12)	C(13)	C(14)	C(15)
−0.01	0.01	0.00	0.00	0.00	0.01

3. BN_4Mo Chelate Ring

Plane V: (1N(1), 2N(1), 1N(2), 2N(2)) $-2.32x + 7.04y + 17.72z - 5.63 = 0$

Deviations of Atoms from Plane

Atoms	1N(1)	2N(1)	1N(2)	2N(2)	Mo	B
Distance	−0.01	0.01	0.01	−0.01	−1.12	−0.75

[a] The equation of the plane has the form $Ax + By + Cz - D = 0$, where x, y, and z are the fractional coordinates.

Results

The atomic positional parameters and anisotropic thermal parameters are listed in Table I, which also lists the coordinates for all the hydrogen atoms which were introduced. Root-mean-square amplitudes of thermal vibration are listed in Table II.

The molecular structure is shown in Figure 1, which also defines the atom numbering scheme. The interatomic dis-

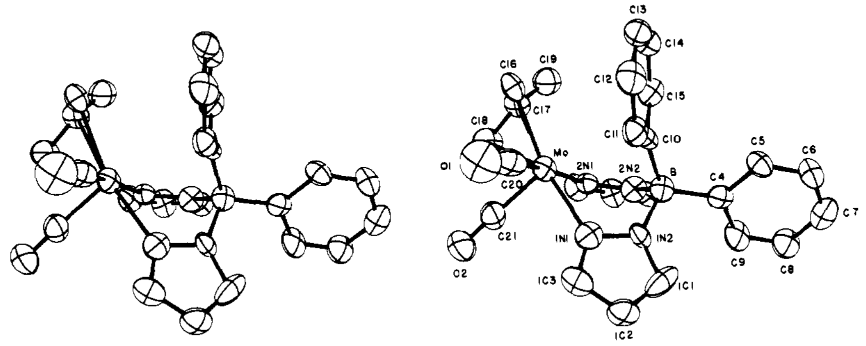

Figure 1. An ORTEP stereoview of $[Ph_2B(pz)_2][\eta^3\text{-}CH_2C(Me)CH_2](CO)_2Mo$. The atom numbering scheme used in all tables is defined. The atoms are represented by 50% probability thermal ellipsoids.

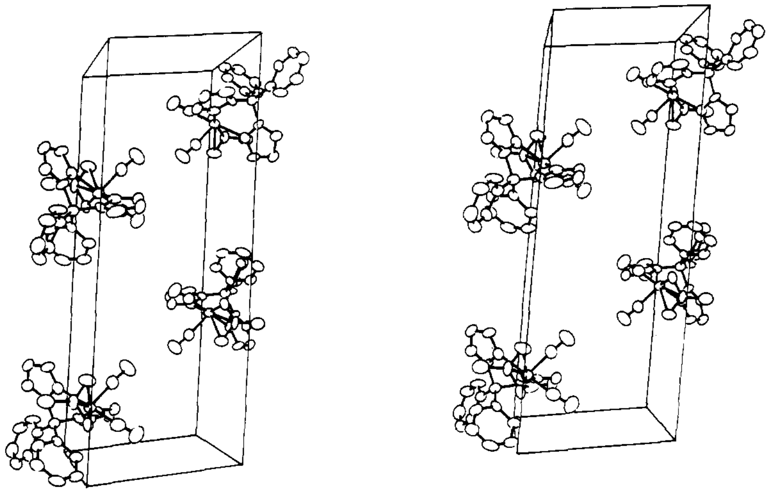

Figure 2. A stereoscopic view of the structure of $[Ph_2B(pz)_2][\eta^3\text{-}CH_2C(Me)CH_2](CO)_2Mo$ showing the unit cell packing. The *a* axis is horizontal, the *b* axis is vertical, and the *z* axis points into the paper. The atoms are represented by 50% probability thermal ellipsoids.

tances are listed in Table III and bond angles are listed in Table IV. Some important molecular planes are described in Table V. The packing of the molecules in the unit cell can be seen in Figure 2. The packing shows no unusual features.

Discussion

Insofar as the set of five ligands, the two pyrazolyl nitrogen atoms, two carbonyl groups, and the η^3-allyl group (regarding it as taking up only one coordination position of the metal) is concerned, the structure is similar to those found in the three compounds having B-H · · · Mo or C-H · · · Mo interactions. These five ligands lie at five of the six vertices of an octahedron. In this case, however, the sixth position, trans to one of the CO groups, is vacant. It is this position which is occupied by the bridging hydrogen atom in each of the other three cases.

The chelate ring is buckled into a boat conformation, with the B to Mo distance (3.24 Å) similar to those in the other compounds where C-H · · · Mo interactions occur, and far shorter than in the cases, viz., $[(pz)_2B(pz)_2](CO)_2(\eta^5\text{-}C_5H_5)Mo$[4] and $[(C_2H_5)_2B(pz)_2](CO)_2(C_3H_5)Mo(C_3N_2H_4)$[11] (B · · · Mo, ca. 3.8 Å), where there is no C-H · · · Mo or B-H · · · Mo interaction. It may also be noted that the interaction of ortho hydrogen atoms of phenyl groups with metal atoms, even to the extent of actual oxidative addition of the C-H groups to the metal atom is a fairly widespread phenomenon.[12]

The question which then asserts itself in view of the facts just summarized is: why does not the appropriate phenyl group rotate by about 90° so as to direct one of its ortho hydrogen atoms into the remaining coordination site of the molybdenum atom and thereby form a C-H · · · Mo bond?

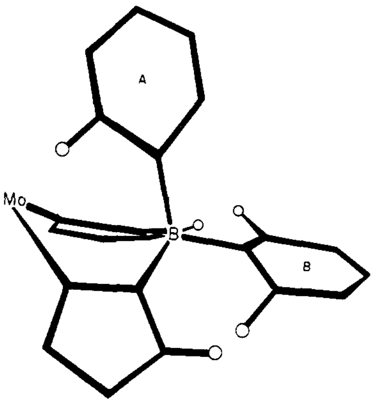

Figure 3. A sketch showing why the orientation of phenyl ring A necessary for a C-H · · · Mo interaction is made impossible by the resultant collisions between hydrogen atoms on phenyl ring B and on the pyrazolyl ring.

The answer to this question is straightforward when a scale model of the structure is examined. Steric factors intrinsic to the satisfactory packing of the four rings, two pyrazolyl and two phenyl, around the boron atom strongly oppose the necessary rotational orientation of the phenyl ring which might supply the C-H bond.

This is illustrated in Figure 3, which shows precisely how the difficulty arises. If the appropriate phenyl ring, A, is oriented so as to allow the C-H · · · Mo interaction, phenyl ring B is forced by the contacts between the other ortho hydrogen atom of ring A and its own ortho hydrogen atoms to rotate so as to make the plane of ring B essentially perpendicular to that of ring A. However, this is also sterically unacceptable since, as shown in Figure 3, severe collisions of both ortho hydrogen atoms of ring B with the hydrogen atoms on the C(1) carbon atoms of the pyrazolyl groups occurs.

It turns out that only the set of ring orientations actually observed, or something very close to it, satisfactorily avoids interference of one or more pairs of hydrogen atoms on the ring carbon atoms two bonds removed from the boron atom. The molecule literally has no choice but to adopt the observed structure and thus to omit the formation of a C-H · · · Mo bond.

Reasons why the chelate ring has a significantly buckled boat conformation are not easy to identify unequivocally, but two possibilities come readily to mind. It seems possible that flattening the chelate ring could lead to increased nonbonded repulsions. It is also possible that there is some weak but not negligible attractive force between the molybdenum atom and the π-electron density of phenyl ring A in the vicinity of carbon atoms C(10), C(11), and C(15). The distances from Mo to the first two are respectively 2.84 and 3.02 Å. At least the first of these may be indicative of some weak donation of π-electron density to the molybdenum atom.

There is one other notable feature of this structure which raises an important general question and that is the very small angles at the phenyl carbon atoms which are attached to the boron atom. These angles are 113 (1)° at C(4) and 115 (1)° at C(10). In addition, two of the angles at the adjacent carbon atoms are significantly larger than 120°, namely, 123 (1)° at C(9) and 124 (1)° at C(15). Such a pattern could result, at least in part, from compressive steric interactions among the four rings due to crowding, although an electronic contribution might also be involved. While electronic factors could be of a complex nature and dependent in some way upon the presence of pyrazolyl as well as phenyl groups on the boron atom, the steric effect, if it is in fact a true cause of the angle contraction or a straightforward electronic effect dependent only on the properties of a B-C bond, should be manifest also in the tetraphenylborate ion. In order to test this hypothesis we have investigated the structure of $RbB(C_6H_5)_4$ and checked the literature for other structural data on the $B(C_6H_5)_4^-$ ion. We find evidence favoring the idea that this type and degree of angle deformation is indeed characteristic of such systems, regardless of whether all four rings are C_6H_6 or not. In $RbB(C_6H_5)_4$ the average of the four angles at the carbon atoms bound to boron is 115.3°.[13]

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Supplementary Material Available. A list of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy of $2.50 for microfiche, referring to code number JACS-75-2118.

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