

tivation energy E_a of 13.7 ± 0.5 kcal mol⁻¹ is obtained. For the molybdenum analog an E_a of 15.3 ± 1.0 kcal mol⁻¹ was obtained. Though it might be argued that these two results are scarcely, if at all, different in a statistical sense, direct comparison of the spectra of the two systems at various temperatures shows clearly that the chromium compound has a significantly lower activation energy than the molybdenum compound since the coalescence temperature of the former is $-30 \pm 5^\circ$ while that of the latter is $+20 \pm 5^\circ$.

It should first be said that the interconversion of gauche and anti rotamers which has been observed need not necessarily be attributed to the process of hindered internal rotation. In view of the remarkable length and concomitant weakness of the Cr–Cr bond, and the fact that at higher temperatures mononuclear radicals apparently exist in equilibrium with the dinuclear molecule, the possibility that the rotamers interconvert by a dissociation–recombination process cannot be dismissed automatically as in the case of rotation about normal C–C bonds. We will, however, continue this discussion on the assumption that non-dissociative rotations occur, since there is no positive evidence to the contrary, but bearing in mind that this assumption could be false.

It is recognized that, in general, the origins of rotational barriers are complex, with both attractive and repulsive forces playing a role. In the present case it is possible that in the staggered conformations there is some stabilizing effect due to interaction between the cis CO groups on one metal atom and the other metal

atom, arising by incipient donation of $d\pi$ electrons from the latter to π^* orbitals of the former.²⁸ However, we think it likely that whatever the reality of such a contribution, the rotational barriers in the $[(\eta^5\text{-C}_5\text{H}_5)\text{-M}(\text{CO})_3]_2$ molecules are primarily repulsive dominated. On this basis, the lower barrier in the chromium compound, compared to the molybdenum one, is then readily understood on the basis of the longer M–M distance in the chromium case.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant No. 33142 and the Robert A. Welch Foundation which provided funds for purchase of the diffractometer and the nmr spectrometer.

Supplementary Material Available. Table I, 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 of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-749.

(28) A significant interaction of this type has been proposed for $\text{Mn}_2(\text{CO})_{10}$ on the basis of semiempirical MO calculations.²⁹ The overall magnitude of the effect in the manganese compound is considerably enhanced over what it *might* be in the chromium compound by (a) the much shorter Mn–Mn distance and (b) the fact that there are eight Mn···C pairs but only four Cr···C pairs.

(29) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

The Interaction of an Aliphatic Carbon–Hydrogen Bond with a Metal Atom. The Structure of (Diethyldi-1-pyrazolylborato)-(trihapto-2-phenylallyl)(dicarbonyl)molybdenum

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Abstract: An interaction between an aliphatic carbon–hydrogen bond and a metal atom which is far stronger than any previously observed in a molecular structure determination is reported. The compound in which this occurs is (diethyldi-1-pyrazolylborato)(trihapto-2-phenylallyl)(dicarbonyl)molybdenum. The α carbon atom of one ethyl group is directed toward the molybdenum atom (C to Mo, 3.06 Å); the rotational orientation about the B–C bond is such as to direct one of the α hydrogen atoms toward the molybdenum. The H···Mo distance appears to be not more than 2.27 (8) Å and possibly as short as about 2.15 Å. A three-center, two-electron bond encompassing the C···H···Mo atoms is postulated to account for this strong interaction and to provide the molybdenum atom with an effective closed-shell configuration. The compound crystallizes in the space group $P2_12_12_1$ with four molecules in the unit cell of dimensions $a = 10.085$ (2), $b = 10.219$ (2), and $c = 20.654$ (4) Å. The anisotropic refinement of 2397 independent reflections with intensities three times greater than their esd's converged at $R_1 = 0.044$ and $R_2 = 0.053$.

There have been enormous strides made in recent years in both the practical development and the mechanistic elucidation of catalytic processes used to transform and synthesize industrial organic chemicals on a large scale. Processes such as hydrogenation, hydroformylation, hydrosilation, and olefin oxidation have been intensively studied with the result that the

broad basic principles, if not all of the fine details, of their mechanisms are now appreciated. In the development of such knowledge a prominent role has been played by the structural characterization of compounds which are presumed to be similar to but less labile than the actual intermediates in the catalytic system itself. Thus, there are stable compounds of platinum, iridium,

Table III. Positional and Temperature Parameters for $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2](\text{CO})_2\text{Mo}^{\text{c}}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^{b}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0.06655 (5)	0.03842 (5)	0.01959 (2)	57.7 (4)	82.6 (4)	16.3 (1)	-1.8 (5)	4.6 (2)	0.3 (2)
1N(1)	-0.1414 (5)	-0.0120 (5)	0.0161 (3)	74 (5)	92 (5)	15 (1)	12 (4)	-2 (2)	6 (2)
1N(2)	-0.2161 (4)	-0.0285 (6)	0.0708 (2)	56 (4)	95 (5)	19 (1)	-13 (5)	-2 (2)	5 (2)
1C(1)	-0.3401 (6)	-0.0606 (7)	0.0540 (4)	55 (6)	121 (8)	30 (2)	-17 (6)	-1 (3)	5 (4)
1C(2)	-0.3469 (7)	-0.0706 (7)	-0.0119 (4)	76 (7)	114 (8)	33 (2)	-19 (6)	-16 (3)	7 (4)
1C(3)	-0.2242 (7)	-0.0403 (8)	-0.0338 (3)	96 (7)	111 (7)	20 (2)	-8 (8)	-11 (2)	6 (3)
2N(1)	-0.0080 (5)	0.1754 (5)	0.0939 (2)	61 (5)	87 (5)	18 (1)	-3 (4)	6 (2)	-1 (2)
2N(2)	-0.1011 (5)	0.1370 (5)	0.1372 (2)	60 (5)	91 (5)	18 (1)	5 (4)	3 (2)	-5 (2)
2C(1)	-0.1462 (7)	0.2417 (7)	0.1694 (3)	96 (7)	110 (7)	24 (2)	11 (6)	6 (3)	-10 (3)
2C(2)	-0.0815 (9)	0.3519 (7)	0.1471 (3)	125 (9)	94 (7)	26 (2)	6 (7)	-1 (4)	-8 (3)
2C(3)	0.0037 (7)	0.3065 (7)	0.1004 (3)	83 (7)	92 (7)	25 (2)	-14 (6)	-2 (3)	1 (3)
B	-0.1466 (7)	-0.0088 (7)	0.1379 (3)	58 (6)	102 (8)	17 (2)	-5 (5)	1 (2)	2 (3)
C(4)	-0.2592 (7)	-0.0335 (9)	0.1935 (3)	88 (7)	134 (8)	25 (2)	2 (8)	10 (3)	8 (4)
C(5)	-0.2072 (9)	-0.0270 (12)	0.2627 (4)	152 (10)	203 (12)	22 (2)	15 (12)	6 (4)	4 (5)
C(6)	-0.0207 (6)	-0.1050 (7)	0.1422 (3)	69 (6)	96 (7)	22 (2)	2 (5)	-2 (2)	9 (3)
C(7)	-0.0503 (8)	-0.2482 (7)	0.1472 (4)	125 (10)	86 (7)	37 (2)	-4 (7)	0 (4)	12 (3)
C(8)	0.2608 (6)	0.1639 (7)	0.0285 (4)	65 (6)	116 (7)	29 (2)	-10 (5)	8 (3)	3 (3)
C(9)	0.2793 (5)	0.0371 (7)	0.0540 (3)	42 (5)	116 (7)	24 (2)	6 (6)	6 (2)	3 (4)
C(10)	0.2706 (7)	-0.0616 (8)	0.0076 (4)	71 (7)	127 (9)	29 (2)	23 (6)	2 (3)	-9 (3)
C(13)	0.3053 (6)	0.0091 (6)	0.1244 (3)	40 (5)	111 (8)	25 (2)	-9 (5)	9 (2)	-3 (3)
C(14)	0.3001 (8)	0.1059 (8)	0.1702 (4)	107 (8)	117 (8)	30 (2)	-7 (7)	-3 (4)	-10 (4)
C(15)	0.3348 (9)	0.0808 (10)	0.2347 (4)	128 (11)	195 (13)	23 (2)	-21 (10)	1 (4)	-12 (4)
C(16)	0.3743 (8)	-0.0425 (12)	0.2533 (4)	92 (8)	213 (13)	24 (2)	-17 (11)	3 (3)	7 (5)
C(17)	0.3792 (8)	-0.1367 (10)	0.2077 (4)	91 (8)	181 (12)	33 (3)	15 (8)	13 (4)	25 (5)
C(18)	0.3466 (7)	-0.1134 (8)	0.1438 (4)	68 (7)	119 (8)	30 (2)	1 (6)	4 (3)	4 (4)
C(11)	0.0666 (8)	0.1654 (6)	-0.0495 (3)	78 (7)	105 (6)	24 (2)	9 (7)	7 (3)	-1 (3)
C(12)	0.0748 (8)	-0.0782 (6)	-0.0545 (4)	91 (7)	104 (7)	25 (2)	3 (7)	4 (4)	-8 (3)
O(1)	0.0638 (6)	0.2357 (6)	-0.0930 (3)	136 (6)	162 (7)	30 (1)	20 (7)	7 (3)	31 (3)
O(2)	0.0772 (7)	-0.1405 (6)	-0.1018 (2)	163 (8)	158 (7)	23 (1)	-2 (7)	4 (3)	-18 (3)
1H(1)	-0.409	-0.056	0.088	5.2 ^c					
1H(2)	-0.411	-0.074	-0.034	5.5					
1H(3)	-0.208	-0.024	-0.078	5.0					
2H(1)	-0.210	0.239	0.206	5.2					
2H(2)	-0.074	0.436	0.158	5.4					
2H(3)	0.054	0.356	0.071	4.8					
4H(1)	-0.330	0.049	0.194	5.5					
4H(2)	-0.281	-0.127	0.188	5.5					
5H(1)	-0.151	0.031	0.277	7.1					
5H(2)	-0.152	-0.109	0.275	7.1					
5H(3)	-0.269	-0.005	0.290	7.1					
6H(1)	0.042 (8)	-0.096 (8)	0.107 (4)	4.9					
6H(2)	0.050	-0.067	0.179	4.9					
7H(1)	0.021	-0.318	0.151	6.0					
7H(2)	-0.078	-0.288	0.114	6.0					
7H(3)	-0.107	-0.290	0.175	6.0					
8H(1)	0.251	0.243	0.059	5.2					
8H(2)	0.280	0.185	-0.011	5.2					
10H(1)	0.271	-0.161	0.022	5.4					
10H(2)	0.287	-0.045	-0.034	5.4					
14H	0.289	0.183	0.163	5.8					
15H	0.336	0.144	0.264	6.8					
16H	0.390	-0.069	0.302	6.6					
17H	0.412	-0.222	0.219	6.7					
18H	0.342	-0.193	0.110	5.3					

^a The numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits. ^b The anisotropic temperature factors are of the form $\exp[-10^4(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^c The anisotropic factors, *B* (Å²), are listed for the hydrogen atoms.

happens that compounds of the required type, *viz.*, $[\text{Et}_2\text{B}(\text{pz})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-allyl})$, had already been reported by Trofimenko,¹⁰ who had also found some spectroscopic evidence that they contain a perturbed C-H group, and who commented on the fact that they, like the H_2B compound, had greater stability than would be expected for a truly 16-electron molybdenum complex.

In a discussion with Trofimenko, it was learned that the most tractable of the known compounds was $[\text{Et}_2\text{B}(\text{pz})_2]\text{Mo}(\text{CO})_2(\eta^3\text{-2-phenylallyl})$, and he generously provided us with a sample. After some difficulties in

(10) S. Trofimenko, *J. Amer. Chem. Soc.*, **90**, 4754 (1968); (b) S. Trofimenko, *Inorg. Chem.*, **9**, 2493 (1970).

growing a suitable crystal, the structure has been determined, and it is reported and discussed here.

Experimental Section

A sample of (diethyldi-1-pyrazolylborato)(*trihapto*-2-phenylallyl)(dicarbonyl)molybdenum, $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$, was kindly supplied by Dr. S. Trofimenko. The synthesis and spectroscopic behavior in solution have been reported earlier.¹⁰ Orange crystals, typically truncated parallelepipeds, were obtained from a solution in thoroughly dried and deoxygenated hexane. On the basis of precession photographs these crystals were found to have Laue symmetry *mmm*, and the systematic absences $h00$ for $h \neq 2n$, $0k0$ for $k \neq 2n$, and $00l$ for $l \neq 2n$ uniquely indicated the space group $P2_12_12_1$ (D_2^4). From diffractometer measurements of high-angle axial reflections, using Mo K α radiation, the unit cell dimensions were found to be $a = 10.085$ (2) Å, $b = 10.219$ (2) Å,

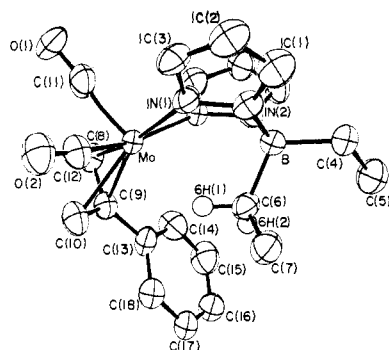


Figure 1. An ORTEP drawing of the molecular structure. The atom numbering scheme used in all tables is defined. The positions of the methylene hydrogens on C(6) obtained in the final cycle of least-squares refinement are indicated by circles of arbitrary size. All other atoms are represented by their 50% probability ellipsoids. Only the front pyrazole ring is labeled. The atoms of the other pyrazole ring are labeled in an analogous fashion but with a number 2 prefixed to each one.

$c = 20.654(4) \text{ \AA}$, and $V = 2128.6(5) \text{ \AA}^3$. The calculated density for $Z = 4$ is 1.47 g cm^{-3} while that measured by flotation in a solution of cesium bromide was $1.45 \pm 0.01 \text{ g cm}^{-3}$.

Diffraction intensities were measured with a Syntex PI computer controlled four-circle diffractometer at $28 \pm 2^\circ$ using Mo $K\alpha$ radiation monochromatized with a graphite crystal. A set of 3257 unique reflections out to $2\theta = 65^\circ$ was collected, employing the θ - 2θ scan technique with a variable scan rate from 2.0 to $24.0^\circ/\text{min}$ and a scan range extending from 1.1° below $2\theta(K\alpha_1)$ to 1.2° above $2\theta(K\alpha_2)$. All data were collected on the same crystal which had the dimensions $0.25 \times 0.25 \times 0.40 \text{ mm}$. Instrument stability and decomposition were monitored throughout the data collection, by regularly remeasuring the intensities of three reflections ($0\bar{1}2$, $20\bar{1}$, $\bar{4}10$). During collection of the first 2300 reflections the check reflections exhibited a steady decrease in intensity, apparent mostly in the $\bar{4}10$ reflection. At this point the crystal was recentered and the data collection was resumed with no significant variation in the intensities of the check reflections. The first data set was corrected approximately by applying a linear least-squares analysis of the check reflections *vs.* time. The two data sets were then scaled together.

Standard Lorentz and polarization corrections were applied to reduce the intensities to relative amplitudes, $|F_o|$. No absorption correction was made since the linear absorption coefficient is only 6.3 cm^{-1} . A reflection was considered to be observed if $F_o^2 > 3.0\sigma(F_o^2)$, where $\sigma(F_o^2)$ is the standard deviation estimated from counting statistics. In this way 860 reflections were classified as unobserved.

Solution and Refinement.¹¹ The position of the molybdenum atom was found from a three-dimensional Patterson function, based on 2109 reflections ($2\theta < 50^\circ$). A structure factor calculation based on the molybdenum atom had a discrepancy index¹² between observed and calculated amplitudes of $R_1 = 0.42$. Two subsequent Fourier maps revealed seven more atoms and gave an R_1 of 0.30. The remaining 21 nonhydrogen atoms were located by a series of least-squares phase refinements and difference Fourier syntheses. A final least-squares refinement on all nonhydrogen atoms employing isotropic thermal parameters and only the reflections for which $2\theta < 50^\circ$ yielded $R_1 = 0.067$ and $R_2 = 0.093$.

The function minimized in all least-squares cycles was $\sum w(|F_o| - |F_c|)^2$. Scattering factors were those of Cromer and Waber^{13a}

(11) The following computer programs were used: DATARED by Frenz for data reductions; FOURIER by Dellaca and Robinson, based on Zalkin's FORADP; NUCLS, a full-matrix least-squares program by Ibers and Doedens, based on Busing and Levy's ORFLS program; PERFECT by Frenz for evaluating structure factors; ORTEP by Johnson for illustrations; ORFFE by Busing, Martin, and Levy and modified by Brown, Johnson, and Thiessen for distances and angles; LIST by Snyder for listing structure factors for publication.

(12) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors, respectively, and $w = 4F_o^2 / \sigma^2(F_o^2)$.

(13) (a) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, in press; (b) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

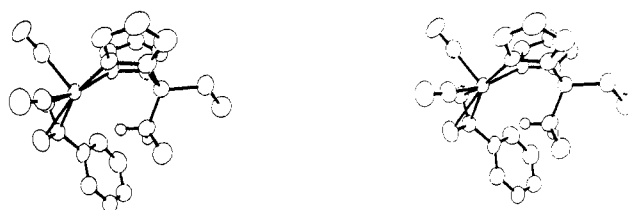


Figure 2. Stereo view of $[\text{Et}_2\text{B}(\text{pz})_2][\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2](\text{CO})_2\text{Mo}$.

except that those of Stewart, Davidson, and Simpson^{13b} were used for hydrogen atoms. Anomalous dispersion corrections¹⁴ were included in the calculated scattering factors for molybdenum.

Refinement was continued using anisotropic temperature parameters for all nonhydrogen atoms and converged with $R_1 = 0.052$ and $R_2 = 0.068$. A difference electron density map revealed the approximate positions of 13 hydrogen atoms, including one at about 2 \AA from the molybdenum atom. The expected coordinates of the remaining 12 hydrogen atoms were calculated and the coordinates of all 25 hydrogen atoms were refined keeping the parameters of the nonhydrogen atoms fixed and assigning isotropic thermal parameters to the hydrogen atoms which were 20% greater than those of the carbon atoms to which they are bonded. Following this a cycle of anisotropic refinement was run in which the hydrogen atom parameters were kept fixed while all other atoms were treated anisotropically.

At this point another difference map was made. It showed no significant features except for four peaks with densities from 0.8 to 2.2 e \AA^{-3} , and all lying at distances of 0.8 – 1.6 \AA from the molybdenum atom. In addition they were at positions which were chemically unreasonable with respect to one or more ligand atoms. While we are dissatisfied by the appearance of these peaks, it does not appear possible that they can be of any structural significance. They may result in part from the inadequacy of the spherical scattering function used for the molybdenum atom.

In order to check whether the correct chirality had been chosen, least-squares cycles of the chosen structure and of its enantiomorph were run using only reflections which were at least ten times greater than their esd's and treating all atoms except molybdenum isotropically. This gave identical R values, bond distances, and bond angles. Furthermore, the set of $F_o(hkl)/F_o(\bar{h}\bar{k}\bar{l})$ as compared to $F_c(hkl)/F_c(\bar{h}\bar{k}\bar{l})$ for each structure showed no significant differences or trends. The two enantiomorphous models are indistinguishable with the data used.

The final refinements were performed on the initially chosen model but the $\Delta f''$ term was omitted in the anomalous dispersion correction for Mo. In the last cycle of refinement, all nonhydrogen atoms were refined anisotropically; the positional parameters of the methylene hydrogen atom nearest to the molybdenum atom were also allowed to vary whereas the parameters of the remaining hydrogen atoms were kept fixed. This refinement converged at $R_1 = 0.044$ and $R_2 = 0.053$. The largest parameter shift, that of the hydrogen atom, is less than 1.2 times its estimated standard deviation. No systematic errors were observed in $\sum w(|F_o| - |F_c|)^2$ as a function of $\sin \theta/\lambda$, F_o , reflection number, or various classes of Miller indices (Table I).¹⁵

Results

Table II, which appears in the microfilm edition,¹⁵ lists the root-mean-square amplitudes of the thermal vibration ellipsoids. The final atomic positional and thermal parameters are listed in Table III.

The structure is depicted in Figure 1. For the sake of clarity, only the two hydrogen atoms on the α -carbon atom close to molybdenum are shown. The atom numbering scheme is defined in Figure 1. A stereo pair which helps considerably to clarify the overall stereochemistry is presented in Figure 2.

The molecule has no element of symmetry. If the allyl group is considered as occupying a single coordination site, located at its center atom, the coordination

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

(15) See paragraph at end of paper regarding supplementary material.

about molybdenum may be described as octahedral. If the CO groups are placed along the $+x$ and $+y$ axes then the 6H(1) atom and one pyrazole nitrogen atom are on the $-x$ and $-y$ axes. The allyl group and the other pyrazole nitrogen atom are on the z -axis positions.

The angles and bond distances in the pyrazolylborate ligand are not unusual in comparison with many others which have been reported (Tables IV and V).^{16, 17}

Table IV. Interatomic Distances (Å)

Atoms	Distance	Atoms	Distance
Mo-1N(1)	2.161 (5)	B-1N(2)	1.566 (8)
Mo-2N(1)	2.209 (5)	B-2N(2)	1.559 (9)
Mo-C(8)	2.349 (7)	B-C(4)	1.635 (10)
Mo-C(9)	2.260 (6)	B-C(6)	1.608 (10)
Mo-C(10)	2.310 (7)		
		C(4)-C(5)	1.524 (11)
Mo-C(11)	1.928 (7)	C(6)-C(7)	1.498 (10)
Mo-C(12)	1.942 (7)		
		C(8)-C(9)	1.411 (10)
Mo-6H(1)	2.27 (8)	C(9)-C(10)	1.393 (10)
		C(8)-C(10)	2.347 (11)
Phenyl ring			
C(13)-C(14)	1.371 (10)	C(9)-C(13)	1.505 (9)
C(14)-C(15)	1.401 (12)		
C(15)-C(16)	1.377 (15)	C(11)-O(1)	1.151 (8)
C(16)-C(17)	1.348 (13)	C(12)-O(2)	1.166 (8)
C(17)-C(18)	1.379 (11)		
C(18)-C(13)	1.379 (10)	C(6)-6H(1)	0.97 (8)
Pyrazolyl Rings ^a			
Atoms	Ring 1	Ring 2	
N(1)-N(2)	1.368 (7)	1.355 (7)	
N(2)-C(1)	1.338 (8)	1.340 (8)	
C(1)-C(2)	1.367 (10)	1.381 (10)	
C(2)-C(3)	1.353 (10)	1.372 (10)	
C(3)-N(1)	1.358 (8)	1.351 (8)	

^a Rings 1 and 2 are identified in Figure 1 by the numbers prefixed to the atom labels.

Ring 2 is planar within experimental uncertainty, no atom deviating more than 0.002 (7) Å from the mean plane. Ring 1, as can be seen in Table VI, appears to have some real but small deviations from planarity. The conformation of the chelate ring in bispyrazolylborate complexes varies from case to case, depending on various factors; that feature of the structure will be considered in the Discussion section.

The carbonyl groups and the allyl ligand display no unusual features. The phenyl group is entirely typical.

The molecules are packed without any abnormal contacts. The shortest intermolecular distance, between 1H(2) and 2H(3), is 2.38 Å, which is about equal to the sum of their van der Waals radii.¹⁸

Discussion

The principal objective of the investigation has been accomplished. It has been shown unequivocally, by direct structural evidence, that in this compound there is an interaction between an aliphatic C-H bond and a metal atom. This is far stronger than any pre-

(16) An extensive survey is given by L. J. Guggenberger, C. T. Pre-witt, P. Meakin, S. Trofimenko, and J. P. Jesson, *Inorg. Chem.*, **12**, 508 (1973), and additional results are found in ref 17.

(17) F. A. Cotton, B. A. Frenz, and A. Stanislawski, *Acta Chim. Inorg.*, **7**, 503 (1973).

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

Table V. Bond Angles (deg)

Atoms	Ring 1	Ring 2	
N(1)-Mo-C(11)	97.8 (3)	95.0 (2)	
N(1)-Mo-C(12)	82.4 (3)	162.0 (3)	
N(1)-Mo-C(8)	160.5 (2)	83.3 (2)	
N(1)-Mo-C(9)	158.5 (2)	96.2 (2)	
N(1)-Mo-C(10)	129.0 (2)	131.1 (2)	
N(1)-Mo-6H(1)	77 (2)	78 (2)	
N(1)-N(2)-C(1)	109.3 (5)	109.4 (5)	
N(2)-C(1)-C(2)	108.8 (6)	108.9 (6)	
C(1)-C(2)-C(3)	105.6 (6)	104.8 (6)	
C(2)-C(3)-N(1)	110.9 (6)	110.5 (6)	
C(3)-N(1)-N(2)	105.2 (5)	106.4 (5)	
Mo-N(1)-N(2)	122.4 (4)	120.7 (4)	
Mo-N(1)-C(3)	132.3 (4)	131.9 (5)	
B-N(2)-N(1)	117.9 (4)	119.1 (5)	
B-N(2)-C(1)	132.7 (5)	131.2 (5)	
N(2)-B-C(4)	106.9 (5)	111.0 (6)	
N(2)-B-C(6)	108.9 (5)	110.6 (5)	
C(13)-C(14)-C(15)	121.0 (8)		
C(14)-C(15)-C(16)	120.3 (8)		
C(15)-C(16)-C(17)	118.0 (7)		
C(16)-C(17)-C(18)	122.4 (9)		
C(17)-C(18)-C(13)	120.5 (8)		
C(18)-C(13)-C(14)	117.7 (7)		
C(9)-C(13)-C(14)	121.5 (7)		
C(9)-C(13)-C(18)	120.5 (6)		
Atoms	Angle	Atoms	Angle
		Mo-C(8)-C(9)	68.8 (3)
N(1)-Mo-2N(1)	81.1 (2)	Mo-C(9)-C(8)	75.7 (4)
C(8)-Mo-C(9)	35.6 (3)	Mo-C(9)-C(10)	74.2 (4)
C(8)-Mo-C(10)	60.5 (3)	Mo-C(9)-C(13)	118.1 (4)
C(8)-Mo-C(11)	72.0 (3)	Mo-C(10)-C(9)	70.3 (4)
C(8)-Mo-C(12)	111.2 (3)		
C(8)-Mo-6H(1)	111 (2)	Mo-C(11)-O(1)	176.1 (6)
C(9)-Mo-C(10)	35.5 (3)	Mo-C(12)-O(2)	175.1 (6)
C(9)-Mo-C(11)	103.7 (3)		
C(9)-Mo-C(12)	101.8 (3)	Mo-6H(1)-C6	136 (6)
C(9)-Mo-6H(1)	81 (2)		
C(10)-Mo-C(11)	102.6 (3)	1N(2)-B-2N(2)	104.2 (5)
C(10)-Mo-C(12)	66.8 (3)	C(4)-B-C(6)	114.6 (6)
C(10)-Mo-6H(1)	85 (2)		
C(11)-Mo-C(12)	80.2 (3)	B-C(4)-C(5)	114.4 (6)
C(11)-Mo-6H(1)	172 (2)	B-C(6)-C(7)	116.3 (6)
C(12)-Mo-6H(1)	105 (2)	B-C(6)-6H(1)	114 (5)
		C(7)-C(6)-6H(1)	106 (5)
C(8)-C(9)-C(10)	113.6 (6)		
C(8)-C(9)-C(13)	123.9 (7)		
C(10)-C(9)-C(13)	122.5 (7)		

viously described C-H...M interaction and it is of the "linear" type, describable as an open $2e-3c$ bond. The general truth of the statements just made can be established without any *direct* evidence as to the location of the interacting hydrogen atom. The carbon to molybdenum distance is 3.06 Å and from the positions of the boron and carbon atoms which flank the carbon atom of interest it is obvious that the hydrogen atom must be close to the C to Mo line. The C-H bond length must be approximately 1.0-1.1 Å, and thus the H...Mo distance must be ~ 2.2 Å, which is vastly shorter than any of the previously observed distances (2.6-2.9 Å).

In fact, the hydrogen atom in question, 6H(1), was actually located and refined isotropically. Its final positional parameters placed it approximately at one vertex of a tetrahedron about the carbon atom, C(6), assuming that two other such vertices are occupied by the boron atom and the methyl carbon atom, C(7). The C(6)-6H(1) distance obtained in the refinement is

Table VI. Weighted Least-Squares Planes^a and Related Parameters

1. Pyrazolylborate Rings						
Equation of Planes						
Plane I Ring 1: $2.62x - 9.86y + 0.94z + 0.23 = 0$						
Plane II Ring 2: $7.17x - 1.32y + 14.28z - 1.05 = 0$						
Deviations of Atoms from Plane						
	N(1)	N(2)	C(1)	C(2)	C(3)	
Ring 1	-0.008 (5)	0.010 (6)	-0.014 (8)	0.005 (7)	0.007 (9)	
Ring 2	-0.001 (5)	0.001 (5)	0.000 (7)	-0.002 (8)	0.002 (7)	
2. Plane III. Phenyl Ring						
Equation $9.57x + 2.50y - 4.12z - 2.44 = 0$						
Atom	C(13)	C(14)	C(15)	C(16)	C(17)	C(18)
Distance	-0.003 (6)	0.001 (8)	0.004 (9)	-0.003 (8)	-0.004 (8)	0.006 (7)
3. BN ₄ Mo Chelate Ring						
Plane IV (Mo, 1N(1), 2N(1))						
Equation $1.47x - 7.093y + 14.559z - 0.111 = 0$						
Plane V (1N(2), 2N(2), B)						
Equation $-7.811x + 2.790y + 8.315z - 2.413 = 0$						
Plane VI (1N(1), 1N(2), 2N(1), 2N(2))						
Equation $6.32x - 7.23y + 6.77z + 0.69 = 0$						
Atoms	1N(1)	1N(2)	2N(1)	2N(2)		
Distance	-0.006 (5)	0.011 (5)	0.009 (5)	-0.008 (5)		
4. Mo Coordination Plane (6H(1), 1N(1), C(11), C(9))						
Plane VII						
Equation $2.09x - 7.44y - 13.50z + 0.42 = 0$						
Atoms	6H(1)	1N(1)	C(11)	C(9)		
Distance	-0.22 (8)	0.000 (5)	-0.001 (6)	0.003 (7)		
Distance of Mo from plane is 0.012 Å						
5. Plane VIII. Allyl Group (C(8), C(9), C(10))						
Dihedral Angles (deg)						
Planes	Angle		Planes	Angle		
I and II	70.1		VIII and I	100.2		
I and III	89.9		VIII and I	125.0		
II and III	59.7		VIII and III	169.8		
VI and IV	144.5					
VI and V	127.5					
Torsional angle [C(7), C(6), B, C(4)] is 50.2(9)°						

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

0.97 (8) Å, together with a Mo–6H(1) distance of 2.27 (8) Å, as shown in Figure 3(a). Thus, if the results of the refinement are accepted *prima facie*, an Mo to aliphatic H distance of 2.27 (8) Å, which is vastly shorter than any such distance previously observed, is demonstrated.

In reality, the Mo···H distance is probably shorter than that. It is well known that in X-ray structures C–H (and other X–H) distances are systematically underestimated by 0.10–0.15 Å. Thus one might argue that the true C(6)–6H(1) distance should be about $0.97 + (0.10-0.15) = 1.07-1.12$ Å. Alternatively, one could invoke the fact that actual aliphatic C–H distances are well established, by spectroscopic methods, to be about 1.10 Å.^{19,20} As a result of the H···Mo interaction, the C–H bond will doubtless be stretched and so a C–H distance as long as 1.13 Å is not at all unlikely. If the direction defined for the C–H bond in the X-ray structure is retained and the C–H distance simply increased to 1.10 Å, the Mo···H distance is then reduced to about 2.15 Å, as indicated in Figure 3(b). We are inclined to believe that this is the best estimate that can be given at this time.

It should be specifically noted that pmr and ir data¹⁰ had already led Trofimenko to suggest an interaction between one or two of the methylene protons and the

(19) D. C. McKean, J. L. Duncan, and L. Batt, *Spectrochim. Acta, Part A*, **29**, 1037 (1973).

(20) "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, No. 18, 18s (1965).

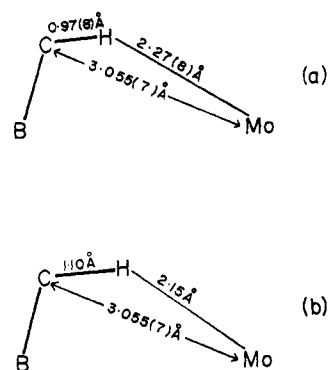


Figure 3. (a) The interatomic distances involving C(6), 6H(1), and Mo obtained by least-squares refinement. (b) C–H and H–Mo distances on the assumption C–H = 1.10 Å while B–C, C–Mo, Mo–B–C, and B–C–H remain the same.

molybdenum atom. It was, of course, not possible to specify in any detail the form or strength of the interaction. The fact that *two* protons had a pronounced upfield shift could have resulted from simultaneous interaction of both with the metal atom or from rapid site exchange between one which is close to Mo and another more distant. The present results strongly imply that the latter is the case. We are carrying out further nmr studies at lower temperatures to verify this directly.

The angle of the C–H···Mo bond is 136 (6)°. The

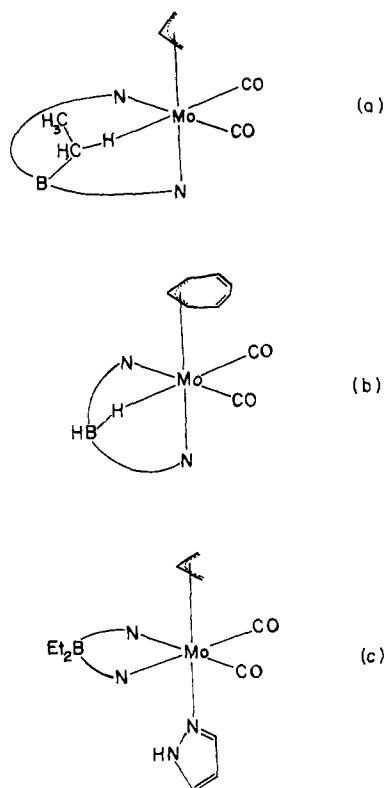


Figure 4. Simplified representations of (a) $[\text{Et}_2\text{B}(\text{pz})_2](\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2)(\text{CO})_2\text{Mo}$, (b) $[\text{H}_2\text{B}(\text{pz})_2](\text{CO})_2(\eta^3\text{-C}_7\text{H}_7)\text{Mo}$, and (c) $[\text{Et}_2\text{B}(\text{pz})_2](\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{pyrazole})\text{Mo}$.

deviation from linearity is doubtless a result of restraints imposed by the geometry of the pyrazolylborate ligand.

The present structure, **1**, invites comparison with those of the related compounds $[\text{H}_2\text{B}(\text{pz})_2](\text{CO})_2(\eta^3\text{-C}_7\text{H}_7)\text{Mo}$ (**2**) and $[\text{Et}_2\text{B}(\text{pz})_2](\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)(\text{pyrazole})\text{Mo}$ (**3**). Schematic representations of the three structures are presented in Figure 4. It is clear that structures **1** and **2** are closely similar; the general way in which the ligands are distributed about the molybdenum atom is qualitatively the same in the two structures.²¹ The only notable difference is in the Mo-N-N-B-N-N ring conformations. In **2**, where

(21) The structure of $[\text{H}_2\text{B}(\text{Mepz})_2](\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)\text{Mo}$ is also of the same type,²² as expected, with an Mo to B distance of about 2.81 Å.

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

a B-H...Mo bond which is about the same length (~ 2.17 Å) as the C-H...Mo bond in **1** exists, the chelate ring is far more buckled.⁹ This is most easily grasped by comparing the Mo to B distances which are 3.290 (7) Å in the present compound, **1**, and 2.797 (5) Å in **2**. Both of these may be compared with the B to Mo distance¹⁷ of 3.806 (4) Å in **3**, where there is no interaction of any atom attached to the boron atom with the molybdenum atom. The chelate ring in **3** is presumably representative of the preferred, unstrained conformation, and **1** and **2** show, respectively, moderate and severe degrees of ring strain, occasioned by the formation of the C-H...Mo and B-H...Mo bonds.

Since B-H bonds are appreciably polar in the sense of H being hydridic, and since coordination of B-H bonds to transition metal atoms occurs widely, we find it reasonable to believe that the strength of the BH...Mo interaction is sufficient to impose considerable distortion on the chelate ring. Almost certainly, a CH...Mo interaction would not be strong enough to do the same, but then, such severe buckling of the chelate ring is unnecessary since the CH bond is inherently in a more favorable position than the BH bond.

Finally, in Figure 4 we note that when a normal ligand, e.g., pyrazole, attacks a molecule of the type **1** forming a donor bond and abolishing the CH...Mo interaction, it does so in a kind of SN2 fashion and finds itself situated, in the product, in a position roughly opposite to the former site of CH...Mo interaction. Concomitantly, there is some twisting of the allyl and CO ligands relative to the pyrazolylborate nitrogen atoms so that the CO groups find themselves trans to the nitrogen atoms.

Acknowledgment. We are indebted to Dr. S. Trofimenko for providing us with the sample used in this study. We are also grateful to Dr. Douglas Collins for his advice and assistance and to Dr. B. A. Frenz for his helpful advice on the use of the computer programs. This research was supported in part by the Robert A. Welch Foundation under Grant No. A494.

Supplementary Material Available. Tables I and II, 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 of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-754.