

COMPLEXES OF POLYPYRAZOLYLBORATE LIGANDS

III*. STRUCTURE OF [DIHYDROBIS(3,5-DIMETHYL-1-PYRAZOLYL)BORATE](η^3 -CYCLOHEPTATRIENYL)DICARBONYLMOLYBDENUM IN SOLUTION

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SUMMARY

Studies of the structure of $[\text{H}_2\text{B}(3,5\text{-Me}_2\text{Pz})_2](\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo}$ and $[\text{Et}_2\text{B}(\text{Pz})_2](\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo}$, where $\text{H}_2\text{B}(3,5\text{-Me}_2\text{Pz})_2$ and $\text{Et}_2\text{B}(\text{Pz})_2$ represent dihydrobis(3,5-dimethyl-1-pyrazolyl)borate and diethyldipyrazolylborate groups respectively, have been carried out on solutions using infrared and PMR spectra. The data indicate that the C_7H_7 groups are *trihapto* and the pyrazolylborate groups are bidentate giving rise to novel complexes that manifest a variety of modes for stereochemical nonrigidity.

INTRODUCTION

Of the many compounds reported by Trofimenko recently¹ one of the most interesting is [dihydrobis(3,5-dimethyl-1-pyrazolyl)borate](cycloheptatrienyl)dicarbonylmolybdenum, $[\text{H}_2\text{B}(3,5\text{-Me}_2\text{Pz})_2](\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo}$ (I). It was considered that at least three structures were plausible for this compound². Assuming an 18 electron configuration for the valence orbitals of molybdenum the C_7H_7 ring might be *heptahapto* or *pentahapto* with the pyrazolylborate ligand being monodentate or bidentate, respectively. Polypyrazolylborate ligands have also been postulated to stabilize molybdenum with a 16 electron configuration², and thus, a *trihapto*- C_7H_7 ring together with a bidentate pyrazolylborate was also considered as a possibility. We have conducted, and report here, infrared, PMR and chemical studies that strongly indicate that the C_7H_7 ring is *trihapto*, and the dipyrazolylborate ligand bidentate. A single crystal X-ray crystallographic study³ shows that this is also true in the crystal. In addition there is an important interaction between the molybdenum atom and one of the hydrogen atoms bonded to the boron atom. Synthesis and spectroscopic study of

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the analogous compound $(Et_2B(Pz)_2](C_7H_7)(CO)_2Mo$ (II) have shown that this system exhibits various types of stereochemical nonrigidity which are reported here.

EXPERIMENTAL

The solvents were dried and purged of oxygen before use. Reactions were carried out in a nitrogen atmosphere. The compounds $KH_2B(3,5-Me_2Pz)_2$ and $NaEt_2B(Pz)_2$ were prepared according to published procedures⁴. $[H_2B(3,5-Me_2Pz)_2](C_7H_7)(CO)_2Mo$ was prepared in the manner described by Trofimenko².

Infrared spectra were taken using a Perkin-Elmer Model 337 grating infrared spectrophotometer and 0.1 mm path-length sodium chloride cavity cells. The PMR spectra were recorded with a Varian HA-100 spectrometer equipped with a variable-temperature probe. Chemical shifts in low and high temperature experiments were obtained by internal referencing with TMS and cyclohexane, respectively. The temperature was measured with an uncalibrated Digitec Digital Thermocouple Thermometer (C-C Type T). Analyses were performed by Meade Microanalytical Laboratories, Amherst, Mass.

$[Et_2B(Pz)_2](C_7H_7)(CO)_2Mo$ (II). The preparative method was closely similar to that described² for $H_2B(3,5-Me_2Pz)_2(C_7H_7)(CO)_2Mo$. THF, DMF and acetone were suitable reaction media. Chromatography on Florisil followed by crystallization of the resultant brown oil (from a CH_2Cl_2 -pentane mixture at -78° gave the analytical sample. The average yield was about 10%. (Found: C, 51.27; H, 5.10; N, 12.37. $BC_{19}H_{23}MoN_4O_2$ calcd.: C, 51.25; H, 5.17; N, 12.58%).

$[H_2B(3,5-Me_2Pz)_2](C_7H_7)(CO)_2Mo \cdot Fe(CO)_5$ (III). 0.6 g of I was dissolved in 200 ml of ether in a 300 ml round-bottom, three-neck flask (pyrex) fitted with a gas inlet, stopper and condenser. To this was added by means of a syringe 20 ml of $Fe(CO)_5$. The solution was irradiated for 10 h with a Hanovia Utility Model Quartz lamp (Cat. No. 30600). After the irradiation the ether and unreacted $Fe(CO)_5$ were pumped off. The residue was extracted with 50 ml of pentane and filtered. The pentane was stripped and the oily residue was chromatographed on Woelm Alumina (neutral, activity 2) in hexane. Elution with benzene yielded the product in 20% yield as a red liquid after evaporation of the benzene. Satisfactory analysis could not be obtained since the liquid decomposed when distilled and retained solvents even after prolonged pumping. It was characterized on the basis of its NMR spectrum and carbonyl stretching spectrum.

RESULTS

Infrared Spectra. The infrared spectra of I and II in the carbonyl region in cyclohexane are shown in Fig. 1. The two sharp peaks of I occur at 1955 and 1875 cm^{-1} , each with a possible error of $\pm 5 cm^{-1}$. The spectrum of II is remarkable for an $M(CO)_2$ species. It consists of two quartets, individual peaks occurring at 1970, 1955, 1945, 1920, 1890, 1880, 1870 and 1840 cm^{-1} . While the basic structure of this spectrum was reproducible, the relative intensities of the sets of bands was strongly dependent on the reaction solvent, temperature and time of reaction, and on the method of work-up. It will be helpful later to recognize that the eight bands can be grouped into 4 pairs. Each band in the high frequency quartet has a counterpart identifiable by its constant

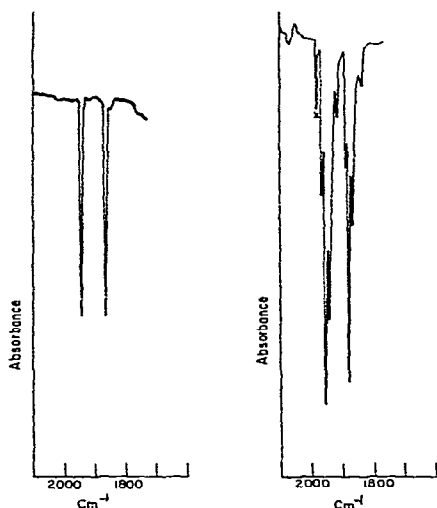


Fig. 1. Portion of the infrared spectra of I (left) and II (right) in cyclohexane.

relative intensity within the lower frequency quartet. This was always found to be true regardless of the variation of relative intensities within each of the quartets.

The infrared spectrum of $[\text{H}_2\text{B}(3,5\text{-Me}_2\text{Pz})_2](\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo} \cdot \text{Fe}(\text{CO})_3$ (III) in the carbonyl region in CS_2 consists of five bands at 2048, 1983, 1972, 1955 and 1878 cm^{-1} , each with a possible error of $\pm 5 \text{ cm}^{-1}$.

Nuclear Magnetic Resonance. The room temperature spectrum of I in toluene is shown in Fig. 2A. The two bands at $\tau 4.6$ and $\tau 4.7$ are assigned to the 4 positions of the pyrazolyl ring. The C_7H_7 resonance appears as a sharp band at $\tau 4.9$. The methyl groups appear at $\tau 7.6$, $\tau 7.7$, $\tau 8.1$ and $\tau 8.2$. Cooling the sample in CS_2 results in broadening and collapse of the C_7H_7 resonance as shown in Fig. 3. The pyrazolyl resonances do not change. Continued cooling leads to the appearance of a broad peak at $\tau 4.2$, a doublet at $\tau 4.75$ and a triplet at $\tau 5.0$. In Fig. 2B and 2C, the effects of heating the sample in mixtures of toluene–benzene (6/1) and toluene–cyclohexane (5/1) respectively, are shown. All six resonances due to the pyrazolyl rings collapse and eventually sharpen to give three resonances at $\tau 4.6$, $\tau 7.68$ and $\tau 8.1$. The C_7H_7 resonance on the other hand becomes sharper as the temperature is raised.

A detailed study of the PMR spectrum of II was not feasible due to the many resonances and their extreme dependence both in chemical shift and relative intensity on the choice of solvent, temperature and time. However, broad resonances due to pyrazolyl and cycloheptatrienyl protons appeared in the right intensity ratio in the regions $\tau 2.0$ to $\tau 4.0$ and $\tau 4.0$ to $\tau 5.5$, respectively. The protons of the ethyl groups appeared as a broad peak from $\tau 9.1$ to $\tau 9.8$. No peaks were observed at τ values greater than 10.

The PMR spectrum of III in CDCl_3 at room temperature consisted of peaks at $\tau 4.3$, $\tau 4.4$, $\tau 5.2$ (broad), $\tau 7.3$, $\tau 7.7$, $\tau 7.9$ and $\tau 8.0$ in the ratio 1/1/7/3/3/3/3. These were assigned to the two protons on the 4 position of the pyrazolyl rings ($\tau 4.3$ and $\tau 4.4$) to the C_7H_7 ring ($\tau 5.2$) and to the methyl protons $\tau 7.3$ to $\tau 8.0$. The variable temperature PMR spectra of III will be reported and discussed together with similar data on analogous compounds, in a future paper.

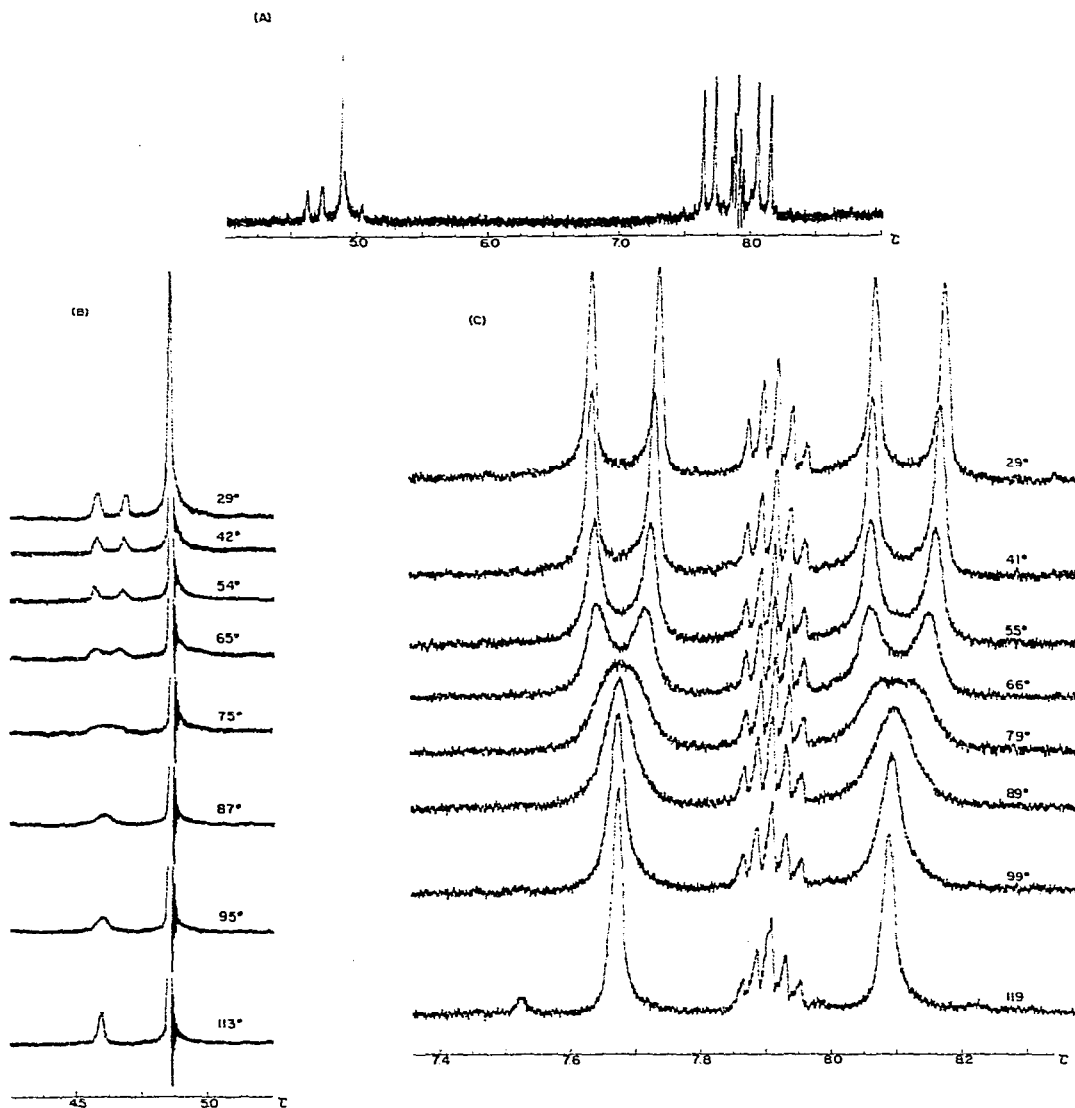


Fig. 2. (A) The PMR spectrum of I in toluene- d_8 . (B) A portion of the PMR spectrum of I in a 5/1 mixture of toluene- d_8 and cyclohexane. (C) The PMR of the methyl region of I in a 5/1 mixture of toluene- d_8 and benzene. The multiplet at $\tau 7.5$ is due to undeuterated toluene. The peak at $\tau 7.5$ is due to decomposition which occurs at about 118° . All spectra at 100 MHz.

Chemical observations. When a cyclohexane solution of I in a Vycor tube is irradiated with a Hanovia high pressure quartz lamp a reaction occurs, which may be followed by observing the gradual decrease of the bands at 1955 cm^{-1} and 1875 cm^{-1} and growth of a new band at 1940 cm^{-1} . At the same time the color of the solution turns from yellow-red to yellow-green. Attempts to isolate the monocarbonyl product by evaporation or by stripping the solvent lead to a further change. A dark green oil that did not absorb in the carbonyl region was isolated. Similar changes were observed in preparing and handling II. Yellow solutions of II had a tendency to turn

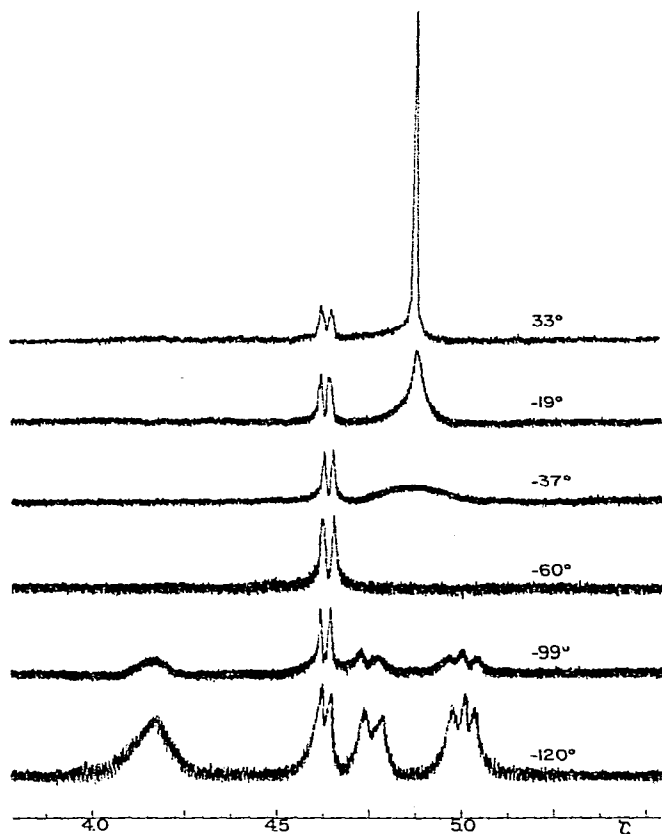


Fig. 3. The PMR spectrum (100 MHz) of I in the C_7H_7 region as a function of temperature in a 5/1 mixture of CS_2 and TMS.

green while changes occurred in its infrared spectrum similar to those just described for I. A band marked "x", appeared at 1990 cm^{-1} at the expense of the bands at 1970 cm^{-1} and 1890 cm^{-1} , (See Fig. 1).

DISCUSSION

Earlier papers^{5,6} in this series have shown the marked tendency of bidentate pyrazolylborate ligands to exist in two boat conformations which interconvert in solution. This interconversion gives rise to extensive variations in the PMR spectrum as the temperature is varied. Furthermore, existence of two boat conformers for BN_4M rings in compounds containing the $M(CO)_2$ group gives rise to splitting of each of the "normal" two CO stretching bands into a doublet, one component of each doublet being due to each of the ring conformers. In the present study we have sought evidence for similar phenomena under circumstances where fluxionality in a different part of the molecule added further complications.

The proposals to be presented below to account for the temperature dependence of the PMR spectra and the multiplicity of CO stretching bands in the infrared spectra are based upon—and are fully consistent with—the assumption that a *trihapto*- C_7H_7

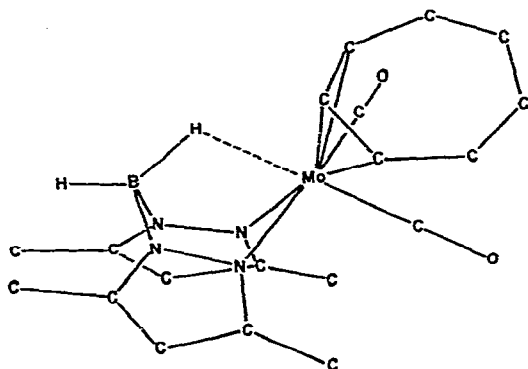


Fig. 4. A schematic representation of the overall structure of I. Only one enantiomorph is shown.

ring is present. This assumption receives independent support from the observation³ that in the crystal I contains an h^3 -C₇H₇ ring and also from the fact that I can form an Fe(CO)₃ adduct in the same way as can $(h^5$ -C₅H₅)(CO)₂Mo(h^3 -C₇H₇)^{7,8}.

For I the crystallographic study³ showed an irregular coordination sphere about the molybdenum (Fig. 4). In an approximate way, however, this arrangement could be described as an octahedron with one CO group in the 1 position and with the 2, 3, 4 and 5 positions occupied by the other CO group, the two coordinated nitrogen atoms and the center of gravity of the coordinated allyl portion of the h^3 -C₇H₇ ring. The sixth position is occupied by a hydrogen bridge bond connecting the boron atom to the molybdenum atom. Such a structure is chiral and, in fact, the asymmetric unit in the crystal is a pair of enantiomeric molecules. With this structural information as a background and possible guide, let us now see how the spectral data for I and II may be interpreted.

Considering the spectral data for I, we first note the striking fact that the infrared spectrum in the CO stretching region at room temperature is merely a doublet in toluene-*d*₈, CS₂ and cyclohexane. This implies that a single combination of BN₄Mo ring conformation and h^3 -C₇H₇ rotational orientation is uniquely stable and is the only one significantly populated at and below ~25°. The PMR spectra at and below room temperature (Fig. 2A and Fig. 3) show that the two pyrazolyl groups are non-equivalent. These observations are all consistent with the molecular structure which I has in the crystal and thus suggest that this structure, or at least one not grossly different from it persists in solution.

The existence of only one conformer of the BN₄Mo ring illustrates the importance of the Mo—H—B interaction. In the case of [B(Pz)₄](h^5 -C₅H₅)(CO)₂Mo the X-ray study revealed that the BN₄Mo ring had a shallow boat conformation⁵. The infrared spectrum of this compound showed splitting in the carbonyl region indicating the presence of the other conformer in solution. However, the BN₄Mo ring in I has a very bent boat conformation. This is undoubtedly due to the 2 electron, 3-center B—H—Mo bond³. This interaction locks the BN₄Mo ring in one conformation even in solution*.

* After the completion of this work a report describing the crystal structure of [H₂B(Me₂Pz)₂](C₃H₅)(CO)₂Mo appeared⁹. This compound exhibits no splitting of its carbonyl bands and a similar metal hydrogen interaction is observed.

The fact that C_7H_7 preferentially takes up one conformation is not surprising. In the case where conformers of a C_7H_7 ring have been observed, $(C_7H_7)(C_5H_5)(CO)_2Mo$, the steric limits imposed by the other ligands in the complex were small compared to those due to the very bulky $H_2B(Me_2Pz)_2$ ligand in I.

The changes observed in the PMR spectrum of I between room temperature and -120° are consistent with the postulate that the $h^3-C_7H_7$ ring is fluxional in the usual way, undergoing eccentric rotation which changes the point of attachment of the metal atom to the ring π system. Previous examples of this include $(h^5-C_5H_5)(h^3-C_7H_7)(CO)_2Mo$ ^{8,10}, $(h^5-C_5H_5)(h^3-C_7H_7)(CO)Fe$ ¹¹ and $(h^3-C_7H_7)(CO)_3Co$ ¹². Only recently has a plausible example of a fluxional *pentahapto*- C_7H_7 ring been reported in the compound $(C_7H_7)(CO)_3Mn$ ¹³. The low temperature limiting spectrum of the manganese complex is very different from those reported for $h^3-C_7H_7$ groups. The similarity of the low temperature spectrum of I to those of other $h^3-C_7H_7$ rings, the occurrence of an $h^3-C_7H_7$ in the crystal structure of I and the apparent retention of this structure in solution indicates that the C_7H_7 ring in I is *trihapto*. It is interesting to speculate that the monocarbonyl product formed by irradiation of I may have an $h^5-C_7H_7$ ring. Further work is underway to explore this possibility.

The changes in the PMR spectrum of I as the temperature is raised to 120° are consistent with the postulate that the enantiomeric forms of I can interconvert. A fast interconversion would result in a time average mirror plane being imposed on

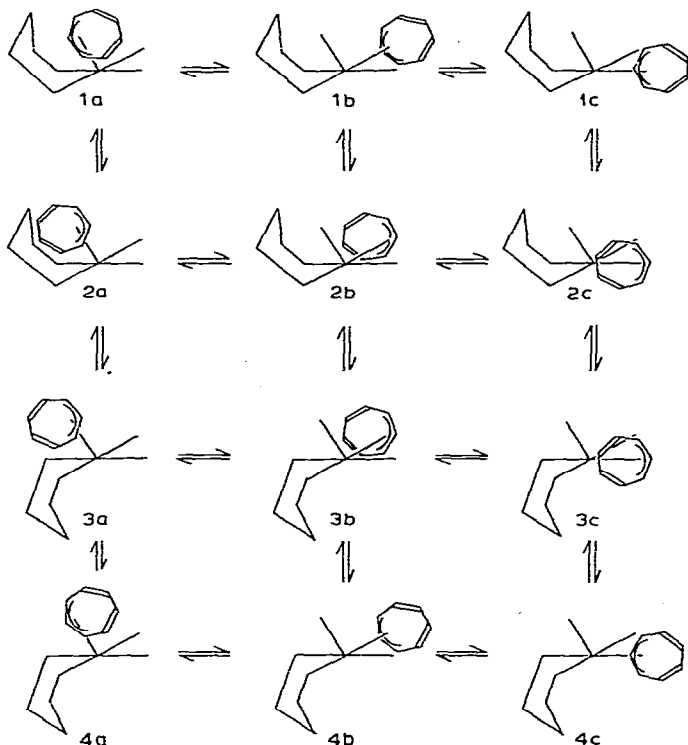


Fig. 5. A diagrammatic representation of the possible structures for compounds of the type I and II. The boat shape represents the BN_4Mo ring of the pyrazolylborate ligand. The carbonyl groups have been omitted.

the molecule. This interconversion is probably achieved by simple rotation of the $\text{H}_2\text{B}(\text{Me}_2\text{Pz})_2$ ligand about the molybdenum. As shown in Fig. 5, a complete rotation would result in three possible positions for the C_7H_7 ring (i.e., 1a, 1b, 1c). All the evidence seems to suggest that the position where the C_7H_7 ring lies between the pyrazolyl ring (i.e., 1a) is never achieved. The actual structures of I are diagrammatically represented in Fig. 5 by structures 4b and 4c. The spectral data reported by Trofimenko² for analogous compounds containing substituted allyl ligands are also consistent with this explanation.

The structures represented in Fig. 5 are those possible when all the conformations of the BN_4Mo ring, the C_7H_7 ring and the rotational isomerization of the $\text{H}_2\text{B}(\text{Me}_2\text{Pz})_2$ ligand about the $(\text{C}_7\text{H}_7)(\text{CO})_2\text{Mo}$ unit are combined. Compound I exists only in structures 4b and 4c because the BN_4Mo ring is locked by the Mo-H interaction and the C_7H_7 ring is restrained from existing in an "endo" type configuration by the bulky nature of the pyrazolyl ligand. However, in compound II these restrictions are not present. The complex infrared spectrum of II in the carbonyl region is consistent with the postulation that there are at least four isomers present. In principle, it would be possible by PMR to discover to which series of isomers (a, or b and c) II belonged. The b and c series would have pyrazolyl resonances in the ratio 1/1 while in the a series they would be identical. However the complexity and instability of II precluded this. The decreased stability of II with respect to I is consistent with the absence of the possibility of forming a 3-center hydrogen bridge bond between the boron atom and the molybdenum atom. The present data on II do not rule out the possibility that the C_7H_7 ring is *pentahapto* but we feel that this is unlikely.

CONCLUSION

The 6-membered BN_4Mo ring and the $h^3\text{-C}_7\text{H}_7$ ring in I do not exhibit their customary tendency to assume two conformations each in solution. Instead one of the 4 possible combinations is highly favoured due to a stabilized M-H interaction which locks the BN_4Mo ring into one deep boat conformation and the bulkiness of the $\text{H}_2\text{B}(\text{Me}_2\text{Pz})_2$ ligand which restricts the $h^3\text{-C}_7\text{H}_7$. However, I exists as enantiomers in the crystal and in solution these enantiomers interconvert at 120° by an intramolecular motion. The BN_4Mo ring and the $h^3\text{-C}_7\text{H}_7$ ring in II however do combine their possible conformations to generate a complete set of 4 conformers which are observed in varying ratios in the infrared.

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