

COMPLEXES OF POLYPYRAZOLYLBORATE LIGANDS

II. CONFORMATIONAL ISOMERISM IN [HYDRIDOTRIS(1-PYRAZOLYL)-BORATE](*h*⁵-CYCLOPENTADIENYL)DICARBONYLMOLYBDENUM AND [DIETHYLBIS(1-PYRAZOLYL)BORATE](*h*⁵-CYCLOPENTADIENYL)-DICARBONYLMOLYBDENUM

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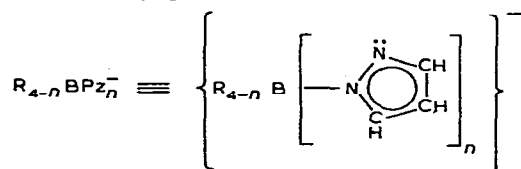
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SUMMARY

Studies of the structures of [HB(pz)₃](C₅H₅)(CO)₂Mo and [Et₂B(pz)₂](C₅H₅)(CO)₂Mo, where HB(pz)₃ and Et₂B(pz)₂ represent the hydridotris(pyrazolyl)borate and the diethylbis(pyrazolyl)borate groups respectively, have been carried out on solutions using infrared and PMR spectra. The data indicate that the pyrazolyl groups coordinate as bidentate ligands to form six-membered rings and that the rings exist in two conformers which interconvert in solution. These studies thus confirm the explanation previously proposed for the temperature dependence of the PMR spectrum of [B(pz)₄](C₅H₅)(CO)₂Mo.

INTRODUCTION

The polypyrazolylborate class of ligands, (1), introduced recently by S. Trofimenko¹, promises to have a large and varied chemistry. The ability of these ligands to stabilize transition metal complexes containing polyolefinic systems makes them interesting in organometallic chemistry. It is noteworthy that a polypyrazolylborate such as tetrakis(1-pyrazolyl)borate ion, [B(pz)₄]⁻, may bind to a metal atom in



(1) R = H or alkyl

1 ≤ n ≤ 4

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various ways depending on the number of pyrazole groups attached. In the previous paper² in this series we reported an investigation of the structure of $[B(pz)_4](C_5H_5)(CO)_2Mo$, (I), by infrared spectra, variable temperature PMR spectra and X-ray crystallography. It was shown that the $B(pz)_4$ ligand is bidentate in this molecule. In addition the infrared red and PMR spectra were found to be consistent with there being conformational isomers of the BN_4Mo ring. In order to gain further information concerning this type of ring conformation phenomenon, which should be of general importance in complexes of bidentate pyrazolylborate complexes, we have investigated the structures of two new compounds: $[HB(pz)_3](C_5H_5)(CO)_2Mo$, (II), and $[Et_2B(pz)_2](C_5H_5)(CO)_2Mo$, (III). We find that the infrared spectra and the variation of the PMR spectra with temperature in these compounds is entirely consistent with the occurrence of conformational isomers similar to those proposed for (I).

EXPERIMENTAL

The solvents, THF and benzene, were dried and purged of oxygen before use by distillation from sodium using benzophenone as an indicator. Reactions were carried out in a nitrogen atmosphere. The compounds $KHB(pz)_3$ and $NaEt_2B(pz)_2$ were prepared according to published procedures^{3,4}. Both $[HB(pz)_3](C_5H_5)(CO)_2Mo$ and $[Et_2B(pz)_2](C_5H_5)(CO)_2Mo$ were prepared by modifications of the method used to prepare $[B(pz)_4](C_5H_5)(CO)_2Mo$ ⁵. Melting points are uncorrected.

$[HB(pz)_3](C_5H_5)(CO)_2Mo$

1.0 g (3.6 mmole) of $(C_5H_5)(CO)_3(Cl)Mo$ and 0.94 g (3.6 mmole) of $KHB(pz)_3$ were dissolved in 40 ml of THF and the solution was refluxed for 3 h. The solvent was stripped and the residue extracted with 40 ml of CH_2Cl_2 . The dark red extract was filtered and the filtrate evaporated to dryness. The residue was chromatographed on a column of acid-washed alumina in hexane. Elution with benzene produced a band that was identified from its infrared spectrum as $[C_5H_5(CO)_3Mo]_2$. Elution with CH_2Cl_2 delivered (II) in approximately 40% yield. The compound was crystallized by cooling a solution in a 1/1 mixture of CS_2 and hexane. M.p. 129° (under N_2). (Found: C, 43.9; H, 3.44; N, 19.5; mol.wt., 437. $C_{16}H_{15}BMoN_6O_2$ calcd.: C, 44.65; H, 3.49; N, 19.53%; mol.wt., 430.)

$[Et_2B(pz)_2](C_5H_5)(CO)_2Mo$

The preparative method was closely similar to that described above and gives a red-orange oil after chromatography. The oil was slightly air-sensitive but, with appropriate precautions, it was recrystallized from a 1/1 mixture of CS_2 and hexane. The yield was approximately 30%. An analytical sample was obtained by subliming freshly chromatographed material at 110° and 0.1 mm. M.p. 130° (under nitrogen). The molecular weight is derived from the parent ion peak observed in the mass spectrum. We thank Miss Norma J. Maraschin for this measurement. (Found: C, 48.51; H, 4.98. $C_{17}H_{21}BMoN_4O_2$ calcd.: C, 48.57; H, 5.00%; mol.wt., 420.)

Infrared spectra were taken using a Perkin-Elmer 337 grating infrared spectrophotometer and 0.1 mm path-length sodium chloride cavity cells. The proton magnetic resonance spectra were recorded with a Varian HA-100 spectrometer equipped with a variable-temperature probe. All chemical shifts were obtained by internal re-

ferencing with TMS except in the case of (II) in toluene where cyclohexane was used as a reference. The temperature in the probe was measured with an uncalibrated Digitec Digital Thermocouple Thermometer (C-C Type T). Analyses were performed by Meade Microanalytical Laboratories, Amherst, Mass.

RESULTS

Infrared spectra

The infrared spectrum of (III) in the carbonyl region in CS_2 is given in Fig. 1. It is a good example of the type of spectrum also observed for (I) and (II). It consists of two doublets, individual peaks occurring at 1970, 1955, 1885 and 1865 cm^{-1} , each with a possible error of ± 5 cm. For (II) in the same solvent the individual peaks occur at 1970, 1955, 1890 and 1810 cm^{-1} , but in this case the bands at 1970 and 1890 cm^{-1} were very much less intense than the others.

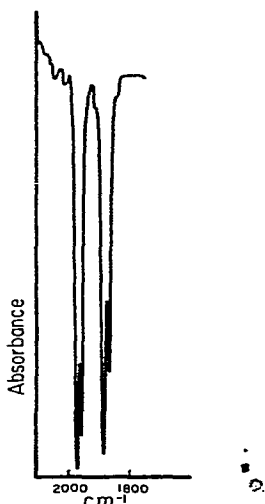


Fig. 1. A portion of the infrared spectrum of $[(\text{C}_2\text{H}_5)_2\text{B}(\text{pz})_2](h^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}$ in CS_2 solution in the CO stretching region.

Nuclear resonance spectra

The PMR spectra of (II) at various temperatures in a mixture of toluene- d_8 and cyclohexane in the ratio 6/1 are shown in Fig. 2. In the spectrum at -49° two sharp lines at τ 5.4 and τ 5.2 can be observed. These bands are in the region where resonances due to the $h^5\text{-C}_5\text{H}_5$ group are usually found. Between τ 4.5 and τ 2.0 a very complex pattern of resonances is observed. Discounting the peak due to incompletely deuterated toluene a total of 12 bands can be counted. These are due to the protons on the pyrazole rings. At room temperature the spectrum of (II) has broadened considerably. All the bands continue to broaden as the temperature is raised until at about 86° the spectrum is almost completely collapsed. Further increase in the temperature causes growth of new bands at about τ 5.3 and between τ 4.5 and τ 2.0. The compound decomposes at about 120° but in the final spectrum at 118° a very much simplified pattern is observed. There is one band in the $h^5\text{-C}_5\text{H}_5$ region and an unresolved pattern for the pyrazoles that suggests the pyrazole protons

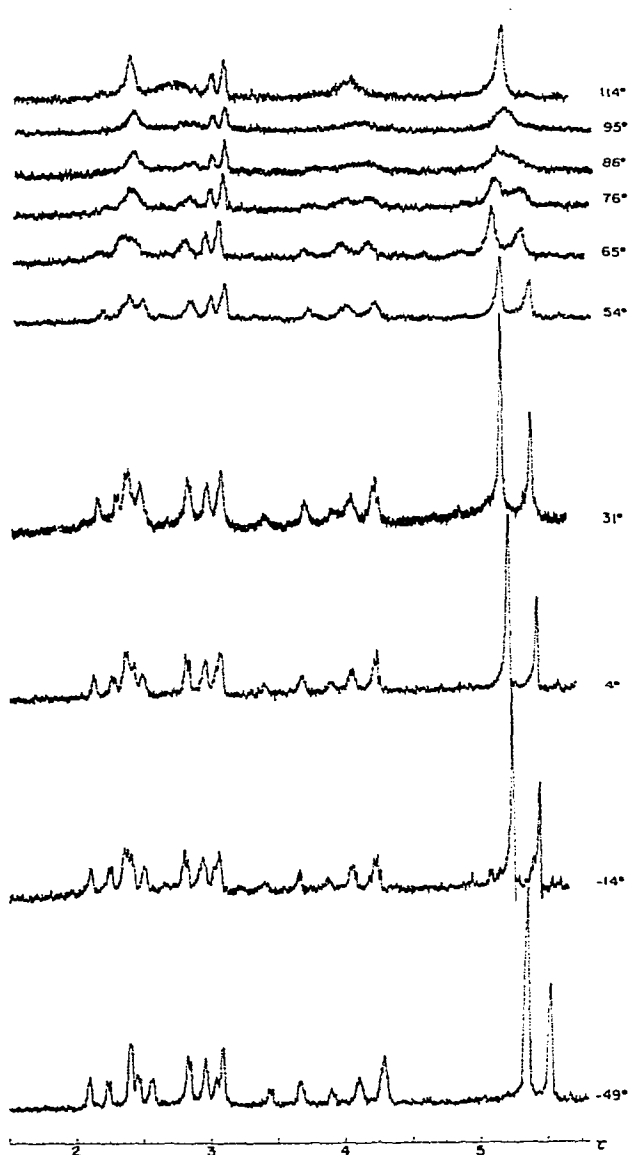


Fig. 2. The proton magnetic resonance spectra (100 MHz) of $[\text{HB}(\text{pz})_3](h^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}$ in toluene- d_8 at various temperatures. The split peak at approximately τ 3 is assigned to incompletely deuterated toluene.

occur in the ratio 2/1. To determine whether significant decomposition had occurred the spectrum was again recorded at room temperature; no change was found.

The PMR spectrum of (III) in a mixture of toluene- d_8 , CDCl_3 and TMS in the ratio 3/2/1 consisted of a sharp band at τ 4.5, which was assigned to the $h^5\text{-C}_5\text{H}_5$ group, a triplet at τ 3.7 and doubled doublets at τ 2.5 and τ 2.2. The resonances due to the ethyl groups appeared as broad peaks at τ 9.3 and τ 9.7. This pattern was invariant with temperature below -100° .

DISCUSSION

If the postulation of the existence in solution of conformational isomers for the BN_4Mo ring in $[\text{B}(\text{pz})_4](\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}$ is correct one might expect isomers of the same type to occur for (II) and (III). The results reported here provide evidence that this is the case. A diagrammatic picture of the possible structures of these isomers is given in Fig. 3. The infrared spectrum of a mixture of the (A) and (B) isomers would be expected to consist of four bands in a pattern of the sort observed in the spectra of (I), (II) and (III). The relative intensities of these bands should depend on the position of the equilibrium between isomer (A) and isomer (B).

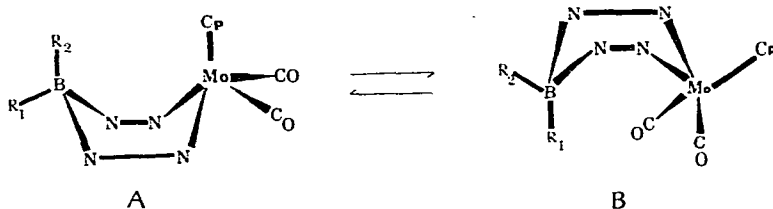


Fig. 3. Diagrammatic representations of the two postulated ring conformation isomers for compounds (I)-(III).

There are now three compounds that display the spectroscopic criteria for the existence of this type of conformational isomerism and some comparisons can be made and interpreted with respect to the steric factors involved. In the case of (III), where $\text{R}_1 = \text{R}_2 = \text{C}_2\text{H}_5$, the equilibrium constant at room temperature, as indicated by the infrared spectrum, is close to 1.0. Moreover, this equilibrium does not seem solvent-dependent since approximately the same ratio of band intensities is observed when the solvents cyclohexane and CS_2 are used. Similarly for (I) where $\text{R}_1 = \text{R}_2 = \text{pyrazolyl}$, the ratio of intensities in toluene- d_8 solvent is close to one. But unlike the case of (III) the equilibrium between the conformational isomers here is very solvent dependent and in fact only one conformer is observed in cyclohexane. This solvent dependence need not be considered surprising in view of the very bulky nature of (pz) groups on boron. In (II) the substituents on boron in the BN_4Mo ring, H and (pz), differ greatly and it is not surprising that the equilibrium between the conformers favors one over the other. One set of bands in the spectrum of (II) is about 10 times as intense as the other set, thus indicating a substantial preference. The equilibrium does not seem to be solvent dependent since about the same ratio is observed in other solvents, such as toluene- d_8 and CS_2 .

It should also be noted that geometrical isomers are possible for (II), since the (pz) group can be *cis* or *trans* to the $h^5\text{-C}_5\text{H}_5$ group. We have looked for evidence of the second of these two isomers but infrared, PMR and chromatographic studies have revealed only one of them. The use of DMF or THF in the synthesis of (II) yielded the same isomer. We do not at this time know which geometrical isomer has been isolated; but it is tempting to speculate that the *trans* isomer might be favored on steric grounds. The observations of only one geometrical isomer which prefers to exist largely in one conformation is not unexpected when the B-substituents are as different as they are in (II).

The variable temperature PMR spectrum of (II) is satisfactorily explained by the postulation of conformational isomers. At -49° the two ringing peaks at τ 5.4 and τ 5.2 are due to the h^5 - C_5H_5 protons in the two isomers. Their peak heights suggest that the conformers exist roughly in the ratio 2/1 at this temperature. In considering the resonances due to the pyrazole groups, we note first that if each of the pyrazole hydrogen atoms in (II) were unique, a total of 18 peaks would be possible; there would be nine peaks from each conformer. If a mirror plane, similar to the one observed in (I) (containing the unbound (pz) ring, the boron atom and the molybdenum atom, and bisecting the C_5H_5 ring and the OC-Mo-CO group) were to exist, each isomer would contribute six bands in the ratio 2/2/2/1/1/1. Since the isomers exist in a 2/1 ratio, the expected 12 bands should be in the ratio 4/4/4/2/2/2/2/2/2/1/1/1. Although an explicit assignment would be very difficult, it is notable that the 12 peaks observed do, in fact, appear roughly in the required ratios.

The spectrum at -49° indicates that the two isomers are not interconverting rapidly on the PMR time scale at this temperature. As the temperature is raised the interconversion is accelerated and all of the bands broaden and collapse. In the fast exchange limit the spectrum should show a single band for the C_5H_5 group and bands corresponding to two pyrazole groups in the ratio 2/1. The fast exchange limit could not be attained in toluene- d_8 due to solvent boiling and in DMF- d_7 the compound decomposes above 120° . Still, the spectrum in toluene- d_8 at 118° clearly shows the growth of one band in the C_5H_5 region and growth of a much simplified pattern in the pyrazole region.

In the previous paper² another possible mechanism for (I) was mentioned, in which rotation of the set of ligands h^5 - C_5H_5 , CO, \leftarrow CO, about a quasi-threefold axis passing through the molybdenum atom is invoked. By a rotation of about 60° , one of the CO groups could be brought into the axial position of the square-pyramidal, "piano stool" structure with the h^5 - C_5H_5 group occupying the position of one of the legs. The question arises as to whether this structure might be one of the "conformers" and the "normal" case with the h - C_5H_5 group in axial position, the other. In the case of (I) the low temperature spectra were complex and not well resolved. However, in the case of (II) the spectra of conformers are well resolved at -49° and we believe the spectra obtained support the "ring-flip" mechanism for the following reason. An unsymmetrical structure with a CO group in the axial position would give rise to nine unique protons. Addition of the six unique protons possible in the structure with the h^5 - C_5H_5 group axial, which contains a mirror plane, gives a total of 15 possible bands in the NMR spectrum. Since the conformers occur in 2/1 ratio, the intensities of these 15 bands should be in the ratios 4(for 3), 2(for 3) and 1(for 9) or 1(for 3) and 2(for 12) depending on which one is favored. Our observation of 12 bands in roughly the ratio 4(3)/2(6)/1(3) at -49° is consistent with the spectrum predicted by the "ring-flip" mechanism.

Very complicated and extensive overlapping of resonances must be postulated to obtain consistency with the "rotation" mechanism. In view of our observation of the solvent dependence of the chemical shifts in these compounds, we feel that the above arguments provide strong though not conclusive evidence in favor of the "ring-flip" mechanism.

The observation that the isomers for (III) could not be "frozen out" in the PMR spectrum prompts a comparison of the exchange rates of the three compounds

(I)–(III), In (I) and (III) the rate of interconversion of the conformation isomers is very fast on the PMR time scale even at low temperatures. Resolution of the isomers in the case of (I) was achieved only at -110° whereas in (III) the isomers were never resolved. But the rate of the analogous process for (II) is very different; even at room temperature the interconversion is slow enough to allow the spectra of two isomers to be observed. In fact, even at 100° the fast exchange limit has not been reached. The reason for these differences is perhaps due to the unsymmetrical nature of the substitution on the BN_4Mo ring in (II), but an explicit explanation is not evident at this time.

CONCLUSION

The occurrence of conformational isomers for the six-membered inorganic metallocycle first observed in $[\text{B}(\text{pz})_4](\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}$ seems to be a general feature of the polypyrazolylborate class of ligand, since it occurs in the two new compounds reported here, $[\text{HB}(\text{pz})_3](\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}$ and $[\text{EtB}(\text{pz})_2](\text{C}_5\text{H}_5)(\text{CO})_2\text{Mo}$.

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