COMPLEXES OF POLYPYRAZOLYLBORATE LIGANDS

I. CONFORMATIONAL ISOMERISM IN [TETRAKIS(1-PYRAZOLYL)-BORATE] (h^5-CYCLOPENTADIENYL)DICARBONYLMOLYBDENUM

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SUMMARY

Studies on the structure of $[B(pz)_4](C_5H_5)(CO)_2Mo$, where $B(pz)_4$ represents the tetrakis(pyrazolyl)borate group, have shown that the $B(pz)_4$ ligand is bidentate, while the cyclopentadienyl group is *pentahapto*. The interesting six-membered metallocyclic ring can exist in two conformers in solution, and these interconvert, with an activation energy of the order of 10 kcal/mol, thus giving rise to extensive variations in the proton NMR spectrum as the temperature is varied.

INTRODUCTION

The recent discovery of the polypyrazolylborate class of ligands has resulted in the synthesis of many new complexes[1]. Tris and tetrakis(1-pyrazolyl)borate ions, ($HB(pz)_3^-$ and $B(pz)_4^-$) have the potential to be tridentate or bidentate. To date no example of these ligands being bidentate to a metal atom has been reported. On the contrary, the tris(1-pyrazolyl)borate ligand is tridentate in $[HB(pz)_3]Mo(CO)_2(NN-C_6H_5)_2$ and in $[HB(pz)_3]_2Co^3$. We wish to report our spectroscopic studies on $[B(pz)_4](C_5H_5)(CO)_2Mo$ (I) which, together with preliminary results from a single crystal X-ray crystallographic study, show the $B(pz)_4$ ligand to be bidentate. Our evidence also suggests that the ring formed by the boron and molybdenum atoms and the two bonded pyrazolyl groups can exist in two conformers which interconvert in solution, thus giving rise to proton NMR spectra which vary markedly with temperature.

EXPERIMENTAL

The complex (I) was prepared according to a previously published procedure[4]. Infrared spectra were taken using a Perkin–Elmer 337 grating infrared spectrophotometer and 0.1 mm path-length sodium chloride cavity cells. Variable temperature proton nuclear magnetic resonance spectra were taken on a Varian HA-100.

RESULTS

Infrared spectra

The infrared spectrum of (I) dissolved in toluene-d_8 in the carbonyl region is

shown in Fig. 1. The spectrum consists of two doublets, individual peaks occurring at 1950, 1935, 1865, 1845 cm^{-1}, each with a possible error of ± 5 cm^{-1}. Thus a total of four bands is observed rather than the expected two. A similar pattern of bands is also
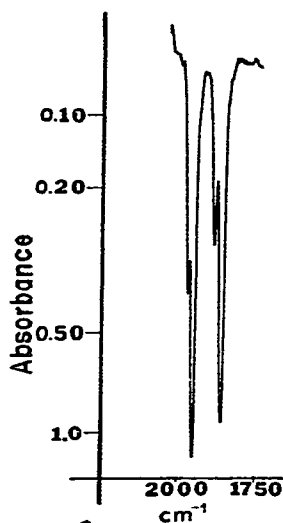

Fig. 1. A portion of the infrared spectrum of $[B(pz)_4](h^5\text{-}C_5H_5)(CO)_2Mo$ in toluene-d_8.

observed when other solvents, such as CS_2, m-xylene, CCl_4 and ether, are used. However, the intensities of the less intense bands at 1950 and 1865 cm^{-1} relative to the intensities of the bands at 1935 and 1845 cm^{-1} are extremely solvent dependent. The ratio of intensities ranges from about 1/20 in CCl_4 to about 1/2 in toluene-d_8. Only one set of bands (i.e., total of two bands) is observed in cyclohexane, in agreement with Trofimenko's report[4].

Nuclear magnetic resonance spectra

The NMR spectra of (I) at various temperatures in a 3/2/1 mixture of toluene-d_8, $CDCl_3$ and TMS are shown in Fig. 2. At room temperature the spectrum consists of a sharp peak at about $\tau 5.2$ which can be assigned to the C_5H_5 group, and a complex group of resonances between τ 4.0 and 2.0 which are due to the protons on the pyrazole rings. Trofimenko pointed out the futility of trying to determine the structure of (I) by NMR[4]. This is especially true in view of our observation of the extreme solvent dependence of the chemical shifts in the pyrazole region. We found the spectrum of (I) to be invariant with temperature from 25° to 150° in DMF-d_7, but when the solution is cooled a number of changes occur. First, the whole spectrum begins to broaden and eventually to collapse. This is first noticeable at about $-69°$ and becomes maximal at about $-92°$. On further cooling to about $-120°$ the spectrum again sharpens and two peaks appear in the C_5H_5 region. At temperatures approaching $-132°$, although viscosity broadening effects may be interfering, it appears that the C_5H_5 resonances have again collapsed while the pyrazole resonances retain some sharpness. Thus, as the temperature is lowered the behavior of the NMR spectrum of (I) may be divided into three stages: (a), broadening and collapse of the whole spectrum; (b), sharpening of the spectrum with concomitant resolution of two C_5H_5 peaks; (c), collapse of the two
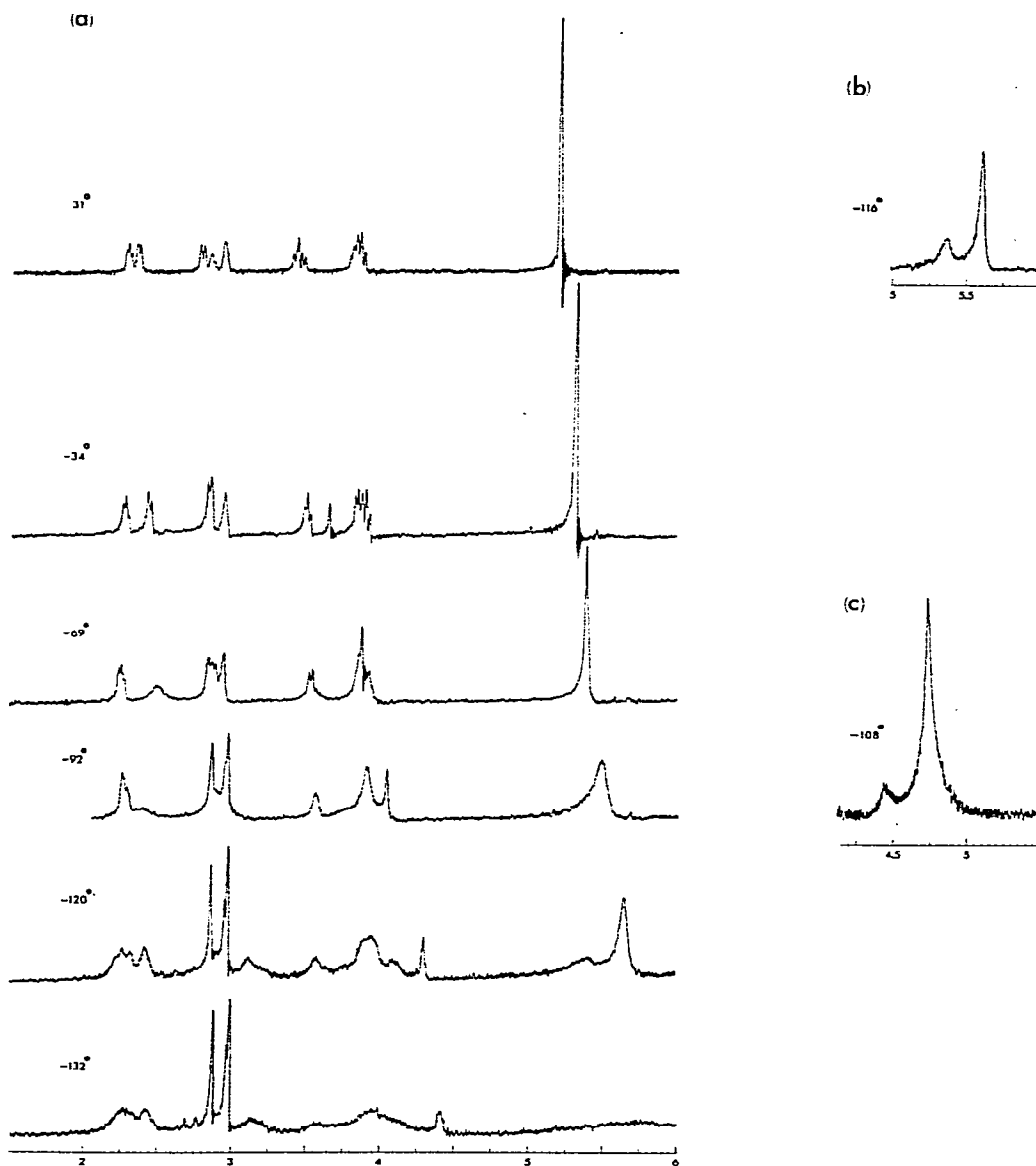
Fig. 2. The PMR spectra of $[B(pz)_4](h^5-C_5H_5)(CO)_2Mo$ in a 3/2/1 mixture of toluene-d_8, $CDCl_3$ and TMS (a) and (b) and in a 3/2/1 mixture of CCl_2F_2, $CDCl_3$ and TMS (c). The peaks at τ 2.7 and τ 2.9 in (a) are due to undeuterated solvent. The scale is in τ units.

C_5H_5 peaks. Stages (a) and (b) have been fully observed using a solvent mixture of CCl_2F_2, $CDCl_3$ and TMS in 3/2/1 volume ratios, but the solution froze in the incipient phase of stage (c).

X-ray crystallographic study
    The molecular structure is presented in Fig. 3. This is based on the preliminary
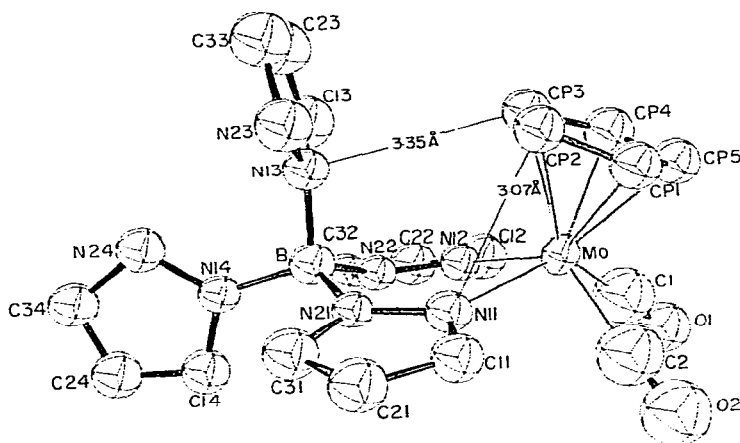
Fig. 3. The [B(pz)₄](h^5-C₅H₅)(CO)₂Mo molecule showing the structure and the atom numbering.

A   B
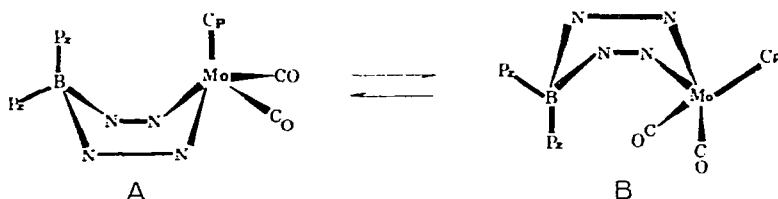
Fig. 4. Possible structures of the conformational isomers of [B(pz)₄](h^5-C₅H₅)(CO)₂Mo.

results of a single crystal X-ray study (see Appendix). The C₅H₅ group is *pentahapto* while the B(pz)₄ ligand is bidentate and forms a six-membered ring with the molybdenum. This structure had previously been proposed[4], with some reservations. The plane formed by the ring of one of the unbound pyrazole groups (pz3) is perpendicular to the line formed by the Mo and the boron. The plane formed by the other unbound ring (pz4) is parallel to the Mo–B line. A mirror plane (non-crystallographic) which contains one unbound ring (pz4), the boron atom and the molybdenum atom and which bisects the C₅H₅ ring and the OC–Mo–CO group can be observed. The six-membered ring formed by the molybdenum and boron atoms and edges of pz1 and pz2 has a boat configuration (see Fig. 4).

DISCUSSION

The spectroscopic results can be explained by postulating the presence in solution of conformational isomers similar to A and B in Fig. 4. 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. It appears that for the cyclohexane solution the equilibrium between A and B is greatly in favor of one conformer. However, in toluene the equilibrium constant is closer to unity. In view of the very bulky nature of the B-substituents on the MoN₄B ring this solvent dependence may not be surprising.

To account for the NMR results, we postulate an interconversion process between A and B. At room temperature the interconversion is rapid with respect to the NMR time scale and an average spectrum is observed; this gives sharp multiplets for

all pz protons and a singlet for C_5H_5. By cooling the solution, the rate of this inter-conversion is diminished, which accounts for the broadening and collapse of the *whole* spectrum [stage (*a*)]. Further cooling reduces the rate of interconversion so much that in stage (*b*) separate spectra for the isomers A and B can be resolved. The most conspicuous manifestation of this is the occurrence of the two resonances at about τ 5 due to the C_5H_5 rings of the two isomers. The complex pattern of the pyrazole region is due to the superposition of the resonances due to the pyrazole protons in the two isomers. Stage (*c*) represents a different phenomenon which we feel affects only the C_5H_5 ring since the resonances due to this group are extensively broadened while at the same time the pz resonances remain fairly sharp. This phenomenon may be the slowing of the rotation of the h^5-C_5H_5 ring. If the structure of (I) in solution is the same at very low temperature as it is in the crystal then it is clear that the h^5-C_5H_5 ring is in a very magnetically asymmetric environment due to the relatively close approach of pz3. Thus the protons of the C_5H_5 ring would have very different chemical shifts if the rotation were stopped which may account for the final broadening of these C_5H_5 resonances as observed in stage (*c*). We have not yet been able to obtain a low temperature limiting spectrum to test this postulate due to experimental difficulties.

We have considered, but rejected, the possibility that the temperature dependence of the NMR spectrum, to the extent that the details of the low temperature spectra are resolved, might be explainable in another way. In this alternative view, the rotation of the set of ligands, h^5-C_5H_5, CO, CO, about a quasi-threefold axis passing through the molybdenum atom is invoked. By a rotation of about 60° one of the CO groups would be brought into the axial position of a square-pyramidal "piano stool" structure with the h^5-C_5H_5 group occupying the position of one of the legs. If this structure were in fact the second structure being observed at low temperatures it should, in principle, be possible to identify it because its lack of symmetry would cause it to have a more complex spectrum than that of either of the "ring flip" conformers. However, the overall complexity and poor resolution of the low temperature spectra do not allow such a decision to be made.

We believe that this "rotational conformer" hypothesis is unlikely for several reasons. Among the vast number of $(h^5$-$C_5H_5)MoL_{4-n}L'_n$ molecules which have been studied there appears to be no case in which the h^5-C_5H_5 ring does not form the "seat" of the piano stool and the ligands L and L' the legs[5]. Another consideration is that in the infrared spectrum of (I) there are no significant differences in the splittings or relative intensities of the symmetric and antisymmetric CO stretching modes of the two conformers. If the two species were the "rotational conformers", in one of which the two CO groups are in quite different environments while in the other their environments are symmetry equivalent, such similarity in the spectra would not be likely. Finally, our work on analogous compounds with simpler NMR spectra, which will be reported in a future paper, provide support for the "ring flip conformer" hypothesis.

CONCLUSION

The postulation of conformational isomers for the rather unique six-membered inorganic metallocycle observed in $[B(pz)_4]$ $(h^5$-$C_5H_5)(CO)_2Mo$ appears to account for all the spectroscopic properties observed. The structural conclusions presented here have been extended in the interpretation of a study of two new compounds, [HB-

TABLE 1

THE OBSERVED AND CALCULATED STRUCTURE FACTORS IN ELECTRONS ($\times 10$)

(pz)$_3$](C$_5$H$_5$)(CO)$_2$Mo and [Et$_2$B(pz)$_2$](C$_5$H$_5$)(CO)$_2$Mo and the analogous C$_7$H$_7$ compounds, reports of which are forthcoming.

ACKNOWLEDGEMENT

APPENDIX

Tetrakis(1-pyrazolyl)boratecyclopentadienyldicarbonylmolybdenum crystallizes in the monoclinic system, and systematic absences indicate the space group C2/c (No. 15). The unit cell dimensions are: $a = 37.09 \pm 0.01$ Å, $b = 8.742 \pm 0.002$ Å, $c = 12.986 \pm 0.005$ Å, $\beta = 93.79° \pm 0.03°$. A unit cell volume of 4201 Å^3 and $Z = 8$ gives

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL

ρ_{calc} 1.57 g·cm^{-3} which agrees well with the experimental value of 1.59 determined by flotation methods. The integrated intensities of 889 reflections within the sphere $\theta \leqslant 65°$ were measured on a General Electric XRD-5 manual diffractometer using nickel-filtered copper radiation and a θ–2θ scan technique. The structure was solved and refined by the usual combination of Patterson, Fourier and least-squares calculations.

With the limited data set and using isotropic temperature factors for all the atoms except the molybdenum atom, the conventional (*i.e.*, unit weighted) *R* factor is 0.086. Though a full data set and subsequent refinement is needed for meaningful discussion of the finer details, the structure of this compound has been unambiguously determined and the accuracy is sufficient for our purposes. No further crystallographic work is planned.

A table of the observed and final calculated structure amplitudes (electrons),

TABLE 2

FINAL ATOMIC POSITIONAL (Å) AND THERMAL PARAMETERS[a]

Atom	x	y	z	$B(\text{Å}^2)$
Mo	0.17994(5)	0.04593(29)	0.21638(15)	[b]
N11	0.1309(5)	−0.0607(29)	0.1463(14)	3.6(4)
C11	0.1232(7)	−0.2122(37)	0.1491(19)	3.9(6)
C21	0.0882(7)	−0.2394(38)	0.1062(21)	4.7(7)
C31	0.0743(7)	−0.0985(38)	0.0690(19)	4.6(6)
N21	0.1008(5)	0.0057(26)	0.0985(14)	2.7(4)
N12	0.1632(5)	0.2362(26)	0.1090(13)	3.2(4)
C12	0.1862(7)	0.3477(40)	0.0846(21)	5.4(7)
C22	0.1665(7)	0.4446(37)	0.0153(20)	5.2(7)
C32	0.1310(7)	0.3889(37)	−0.0016(20)	4.8(6)
N22	0.1311(5)	0.2591(26)	0.0600(14)	3.1(4)
N13	0.0835(5)	0.2446(29)	0.1896(16)	3.8(4)
C13	0.0633(7)	0.1785(37)	0.2595(22)	5.1(7)
C23	0.0523(7)	0.2986(43)	0.3245(22)	5.9(7)
C33	0.0698(8)	0.4207(42)	0.2903(25)	6.3(8)
N23	0.0888(6)	0.4027(35)	0.2054(20)	6.5(7)
N14	0.0651(5)	0.2137(24)	0.0035(14)	3.1(4)
C14	0.0677(5)	0.1638(26)	−0.0952(15)	4.2(5)
C24	0.0359(7)	0.2065(35)	−0.1405(19)	4.5(6)
C34	0.0145(6)	0.2045(34)	−0.0798(20)	4.3(6)
N24	0.0336(6)	0.2893(33)	0.0158(18)	4.1(6)
B	0.0950(9)	0.1821(46)	0.0841(25)	3.8(8)
C1	0.2231(9)	0.0819(41)	0.1640(25)	7.7(9)
O1	0.2525(5)	0.0960(25)	0.1211(15)	7.0(5)
C2	0.2014(9)	−0.1481(50)	0.1679(26)	7.8(10)
O2	0.2149(6)	−0.2578(32)	0.1455(17)	8.2(7)
CP1	0.1783(7)	−0.0500(35)	0.3822(18)	4.3(6)
CP2	0.1465(6)	0.0463(37)	0.3703(18)	4.1(6)
CP3	0.1570(7)	0.1969(36)	0.3499(18)	4.2(6)
CP4	0.1967(7)	0.2023(38)	0.3525(20)	4.9(7)
CP5	0.2092(7)	0.0487(39)	0.3747(19)	4.5(6)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed. [b] The molybdenum atom was assigned an anisotropic thermal tensor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The tensor components with their e.s.d.'s in parentheses are: $\beta_{11} = 0.00046(1)$, $\beta_{22} = 0.00911(53)$, $\beta_{33} = 0.00564(15)$, $\beta_{12} = 0.00004(11)$, $\beta_{13} = 0.00010(3)$, $\beta_{23} = 0.00034(27)$.

multiplied by 10, for $[(C_3H_3N_2)_4B]Mo(CO)_2(C_5H_5)$ is presented as Table 1. The molecular structure and atom numbering system are shown in Fig. 3. Final atomic positions and thermal parameters are given in Table 2, with the listed standard deviations being derived from the inverse matrix of the final least-squares refinement cycle. Intramolecular distances and bond angles are given in Table 3 and 4, respectively.

The most significant result of this investigation is the unequivocal demonstration that in the crystalline state the $[B(pz)_4](C_5H_5)(CO_2)Mo$ molecule has a structure which contains a bidentate tetrakis(1-pyrazolyl) ligand, this being the first structural characterization of the ligand acting in this manner. There is also a slightly tilted *pentahapto*-cyclopentadienyl ring, and two carbonyl groups of the normal terminal type.

The six-membered ring formed by the molybdenum atom, the nitrogen atoms

TABLE 3

INTRAMOLECULAR BOND DISTANCES[a] (Å)

Atoms	Distance	Atoms	Distance
Mo–CP1	2.31(2)	N13–C13	1.35(3)
Mo–CP2	2.42(2)	C12–C23	1.42(3)
Mo–CP3	2.38(2)	C23–C33	1.34(3)
Mo–CP4	2.29(2)	C33–N23	1.36(3)
Mo–CP5	2.26(2)	N23–N13	1.40(3)
Mo–C1	1.80(4)	CP1–CP2	1.44(3)
Mo–C2	1.99(4)	CP2–CP3	1.40(3)
Mo–N11	2.18(2)	CP3–CP4	1.47(3)
Mo–N12	2.23(2)	CP4–CP5	1.44(3)
N11–C11	1.36(3)	CP5–CP1	1.44(3)
C11–C21	1.40(3)	C1–O1	1.26(3)
C21–C31	1.40(3)	C2–O2	1.13(3)
C31–N21	1.37(3)	B–N21	1.56(3)
N21–N11	1.37(3)	B–N22	1.54(3)
N12–C12	1.35(3)	B–N13	1.56(3)
C12–C22	1.40(3)	B–N14	1.50(3)
C22–C32	1.40(3)	N14–C14	1.36(3)
C32–N22	1.39(3)	C14–C24	1.34(3)
N22–N12	1.33(3)	C24–C34	1.34(3)
		C34–N24	1.39(3)
		N24–N14	1.36(3)

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed.

TABLE 4

BOND ANGLES[a]

Atoms	Angle (Deg.)	Atoms	Angle (Deg.)
N12–Mo–N11	82.5(8)	CP1–CP2–CP3	109(2)
Mo–N11–N21	129(2)	CP2–CP3–CP4	109(2)
N11–N21–B	125(2)	CP3–CP4–CP5	106(2)
N21–B–N22	110(2)	CP4–CP5–CP1	109(2)
B–N22–N12	126(2)	CP5–CP1–CP2	107(2)
N22–N12–Mo	128(2)	N14–B–N13	108(2)
C1–Mo–C2	69(1)		
N11–Mo–C1	130(1)		
N11–Mo–C2	81(1)		
N12–Mo–C1	81(1)		
N12–Mo–C2	123(1)		

[a] Numbers in parentheses are the estimated standard deviations occurring in the last digit listed.

on the bonded pyrazole rings, and the boron atom is in a rather flattened boat conformation. The angle subtended at the molybdenum atom is much more acute than the one at the boron atom; this presumably helps to minimize non-bonded repulsions.

The $(h^5\text{-}C_5H_5)$ group is somewhat unusual. The molybdenum to carbon distances fall in the range 2.26 to 2.42 Å; a tilt on the Mo-$(h^5\text{-}C_5H_5$ centroid) vector can account for the variations in the bond lengths. Although the variations are large, this situation is not to be confused with the one found in $(C_5H_5)_3MoNO$ where the Mo–C distances to two of the rings vary from 2.32 to 2.68 Å, a range of almost 0.40 Å. In this case a form of bonding basically different from that of a true $(h^5\text{-}C_5H_5)$ is believed to exist.

The coordination around the boron atom is roughly tetrahedral as anticipated. This type of structure is consistent with the temperature-dependent NMR spectrum of this substance in solution.

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