Attainment of an Eighteen-electron Configuration by Means of Hydrogen Bridging in a Purported Sixteen-electron Pyrazolylborate Complex of Molybdenum; The Structure of (3,5-Dimethylpyrazolylborato)dicarbonyl-*trihapto*-cycloheptatrienyl)-molybdenum

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Summary The structural and dynamic properties of $[H_2B(3,5\text{-dimethylpyrazolyl})]Mo(CO)_2C_7H_7$, studied by X-ray crystallography and spectroscopy, show that the molecule is asymmetric with a *trihapto*-C_7H_7 ring, a severely bent boat form of the chelate ring, and a 2-electron, 3-centre B–H–Mo bond.

Trofimenko has reported a variety of complexes[1] of the polypyrazolylborate ligands, $[R_nB(1\text{-pyrazolyl})_{4-n}]^-$. Those of molybdenum, of the type $[H_2B(3,5\text{-dimethylpyrazolyl})]$-$Mo(CO)_2L$ (L = allyl or C_7H_7) were of special interest since they might have a 16-electron configuration at the molybdenum atoms,[2] but they were much less reactive than might be expected from such an 'electron shortage'. For compound (I) (L = C_7H_7) the presence of an Mo–(*pentahapto*-C_7H_7) fragment instead of Mo–(*trihapto*-C_7H_7) was considered.[2] We have investigated the C_7H_7 compound, both in solution (i.r. and n.m.r.) and by X-ray crystallography and can now present an explanation of the apparent 'electron shortage' and of the dynamic behaviour of this molecule in solution.

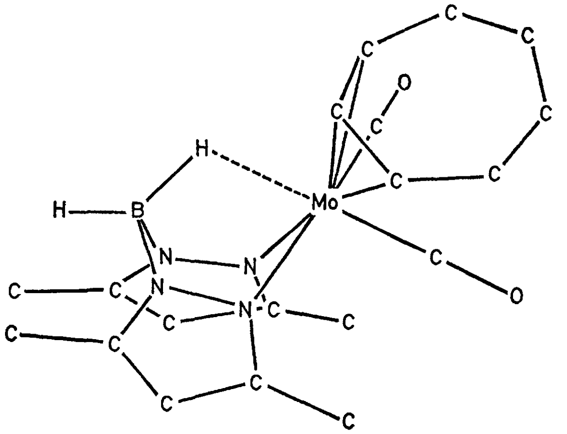

Figure 1. *A schematic representation of the overall structure. Only one enantiomorph is shown.*

The compound crystallizes in space group $P\bar{1}$, $a = 10{\cdot}354(4)$, $b = 19{\cdot}783(8)$, $c = 10{\cdot}318(5)$ Å; $\alpha = 96{\cdot}83(2)°$, $\beta = 86{\cdot}93(2)°$, $\gamma = 107{\cdot}16(1)°$; $Z = 2$. The two molecules in the asymmetric unit cell are approximately enantiomorphous. The structure of one enantiomorph is shown schematically in Figure 1. The structure has been refined to $R_1 = 0{\cdot}032$ and $R_2 = 0{\cdot}045$ using 4998 independent reflexions (Mo-K_α radiation). All 46 hydrogen atoms were located and refined with isotropic thermal parameters. Refinement is continuing; small shifts of hydrogen atoms may occur, but no important changes are to be expected. The C_7H_7 ring is bound in *trihapto*-fashion. The pyrazolylborate chelate ring has a very severely bent boat conformation. We have previously found a much flatter boat conformation in $(Bpz_4)Mo(CO)_2$(*pentahapto*-C_5H_5).[3] A boat conformation is natural to such a ring, but the severity of the puckering in the present case is exceptional. The bending is so great that the boron lies at an average of only 2·81 Å from the molybdenum atom, probably owing to a B–H–Mo two-electron three-centre bond. Distances involving hydrogen atoms in the two independent molecules are shown in Figure 2. Each B–H and Mo–H distance has an e.s.d. of 0·06 Å. The analogous pairs of distances in the two molecules each differ by less than this.

The short B–H(terminal) bonds, long B–H(bridge) bonds and short H–Mo distances are consistent with an unsymmetrical B–H–metal 2-electron bond, comparable to those in some BH_4^- and $B_3H_8^-$ complexes.[4] The molybdenum atom can be considered to achieve an effective 18-electron configuration when the two electrons in the bonding orbital that extends over the B–H–Mo group are considered. The previously puzzling stability of the '16-electron' configuration is thus explained.

After completion of our work, the structure of $[H_2B(2,3\text{-dimethylpyrazolyl})_2]\text{-}Mo(CO)_2C_3H_5$ was reported.[5] A similar severely bent boat configuration of the chelate ring was found, with a B • • • Mo distance of 2·80 Å. However, the hydrogen atoms were not well located in this study and it does not afford a strong case for B–H–Mo bridge bonding (as opposed to mere blocking of Mo by BH_2) although the authors mentioned this possibility.

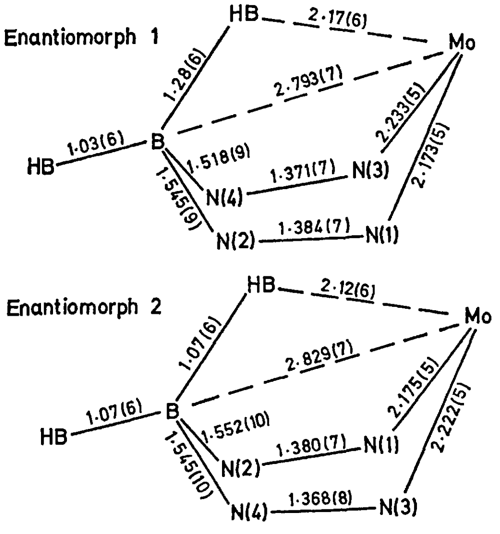

Figure 2. *The* B–H–Mo *two-electron three centre bonding in each of the two enantiomorphs.*

The i.r. spectrum of (I) in solution has only two sharp CO stretching bands, showing that the chelate ring conformation is rigid (due to the B–H–Mo bond) and also that the orientation of the C_7H_7 ring is fixed. Chemically the *trihapto* nature of the Mo–C_7H_7 bonding is shown by the reaction of (I) with $Fe(CO)_5$ under u.v. irradiation to yield a derivative in which $Fe(CO)_3$ is bound to the butadiene residue of the *trihapto*-C_7H_7 ring.

The n.m.r. spectrum of (I) varies markedly with temperature, but the changes are all explicable in terms of the structure. At 25° and below the pyrazolyl groups are not equivalent, giving 2 ring-proton resonances and 4 methyl resonances, as expected from the asymmetric molecular structure. At 25° the C_7H_7 resonance is a sharp singlet which collapses on cooling. At $-120°$ the C_7H_7 ring protons give a pattern typical for a *trihapto*-C_7H_7 ring,[6] and different from that recently reported for a *pentahapto*-ring.[7]

As the temperature is raised the pyrazolyl resonances collapse and by *ca.* $+115°$ the spectrum is consistent with the presence of equivalent rings. A fast interconversion of the enantiomorphs is thus implied at higher temperatures. This could be achieved by a simple internal rotation or by detachment of the B–H–Mo bond to yield a pseudorotating '5-co-ordinate' intermediate.

(*Received*, 27*th March* 1972; *Com.* 514.)

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