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Preliminary communication

THE STRUCTURAL ASPECTS OF ORGANOBORANE AND ORGANOBORATE COMPOUNDS CONTAINING THE (C_6H_4-2-CH_2NMe_2) LIGAND

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Summary

The new organoborates $(ArBMe_3)Li \cdot OEt_2$ (I), $(ArBEt_3)Li \cdot OEt_2$ (II) and $[ArPh(BBN)]Li \cdot OEt_2$ (III) ($Ar = C_6H_4$-2-(CH_2NMe_2), BBN = 9-borabicyclo-[3.3.1]nonyl) were synthesized. The structures of I, II and III and their temperature-dependent dynamic properties were established by means of ^1H, ^{13}C and ^{11}B NMR spectroscopy. It was revealed that I, II and III exist in solution as undissociated molecules with the boron and lithium atoms bonded through alkyl and/or aryl bridges.

The new organoborates I, II and III were synthesized in the reaction:

$$ArLi + BRR'_2 \xrightarrow[\text{room temp.}]{Et_2O} \underset{(I\text{—}III)}{(ArBRR'_2)Li \cdot OEt_2} \qquad (1)$$

(I: R = R' = Me; II: R = R' = Et; III: R = Ph, BR'_2 = 9-borabicyclo[3.3.1]nonyl)

The ^1H NMR spectra of I, II and III are solvent- and temperature-dependent. The protons of the methylene group NCH_2 as well as those of the methyl group NCH_3 have a non-equivalent magnetic environment. At low temperature, the NCH_2 protons exhibit an AB pattern and the signal of the NCH_3 protons splits into two singlets. These spectral phenomena can be explained in terms of the inversion of the configuration at the unsymmetrical C(1) of the aromatic ring and the occurrence of the inversion of configuration of the nitrogen atom, after splitting the donor—acceptor bond between the nitrogen and lithium atoms [1,2].

The spectra of $(ArBMe_3)Li \cdot OEt_2$ provide proof of the occurrence of alkyl-

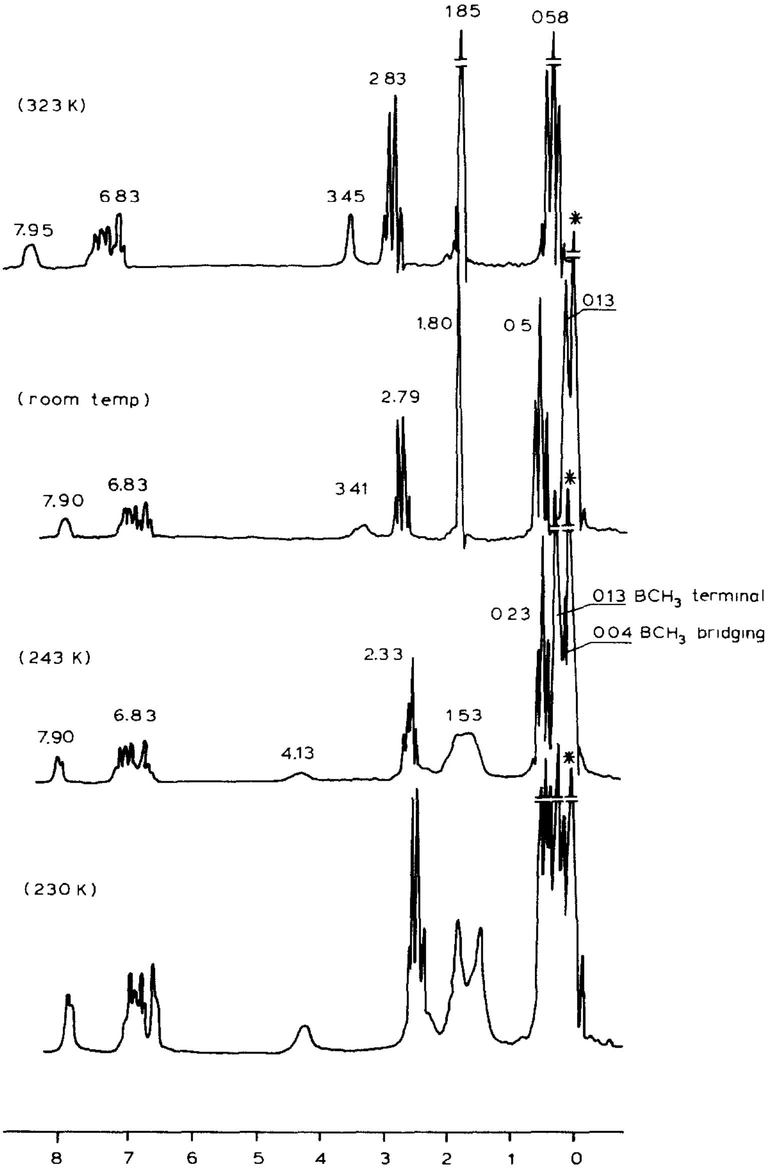

Fig. 1. ^{1}H NMR spectra (δ ppm) of I in toluene-d_8 at various temperature.* TMS, internal standard.

carbon bridges in a borate molecule (Fig. 1). At 243 K, two signals for the B-CH_3 protons are visible and have been assigned to bridging and terminal methyl groups.

The ^{11}B NMR measurements revealed signals for II and III at −12.8 ppm ($BF_3 \cdot OEt_2$ 0 ppm) which confirm that our compounds have a "borate" character and that a negative charge is transferred onto the boron nucleus.

As a result of our investigations, we propose a new structure for organoborate compounds, which is illustrated by the structure of $(ArBMe_3)Li \cdot OEt_2$ (Fig. 2).

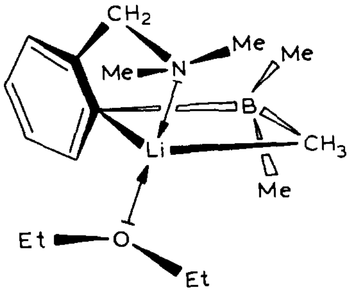

Fig. 2. Proposed structure of I.

References

1 J.T.B.H. Jastrzebski, G. van Koten, M. Konijn and C.H. Stam, J. Am. Chem. Soc., 104 (1982) 5490.
2 G. van Koten and J.G. Noltes, J. Organomet. Chem., 171 (1979) C39; 174 (1979) 367.