Radical Anion of 1,4-Diborabenzene[1]

By Wolfgang Kaim and Hans Bock

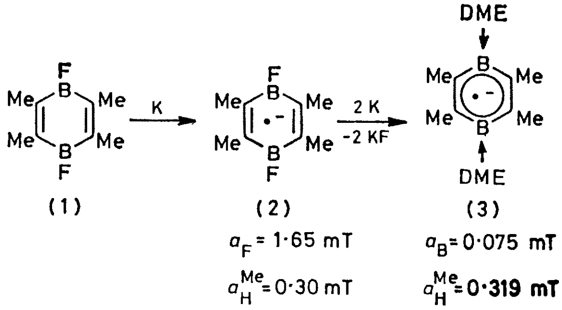
(*Department of Chemistry, Johann-Wolfgang-Goethe-Universität, Niederurseler Hang,* D-6000 *Frankfurt/Main, Federal Republic of Germany*

and Pelham Hawker and Peter L. Timms

(*School of Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Reduction of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene using potassium in dimethoxyethane proceeds in two steps: firstly, the acquisition of one electron yields the unstable radical anion $[\mathrm{FB(MeC{=}CMe)_2BF}]^{-\cdot}$, isoelectronic with durosemiquinone; and secondly the potassium film removes the fluorine substituents and the radical anion $[\mathrm{B(MeC\text{-}CMe)_2B}]^{-\cdot}$ is produced which is stable at room temperature and represents a novel heterocycle, tetramethyl-1,4-diborine.

Radical ions, $(\mathrm{M})^{+\cdot}$ and/or $(\mathrm{M})^{-\cdot}$, are sometimes more easily formed than the corresponding neutral parent molecule, M, which may even be unknown. There are familiar examples among the Huckel-type π-radical ions;[2] more recently published e.s.r. investigations include the tetrasilylbutatriene species, $[(\mathrm{R_3Si})_2\mathrm{C{=}C{=}C{=}C(SiR_3)_2}]^{+\cdot}$ and $[(\mathrm{R_3Si})_2\mathrm{C{=}C{=}C{=}C(SiR_3)_2}]^{-\cdot}$, obtained by redox-cleavage reactions from the neutral hexasilylbut-2-yne, $(\mathrm{R_3Si})_3\mathrm{C\text{-}C{\equiv}C\text{-}C(SiR_3)_3}$.[3]



(1)

(2)
$a_F = 1{\cdot}65$ mT
$a_H^{Me} = 0{\cdot}30$ mT

(3)
$a_B = 0{\cdot}075$ mT
$a_H^{Me} = 0{\cdot}319$ mT

Scheme 1.

We report that on reduction of 1,4-difluoro-2,3,5,6-tetramethyl-1,4-diboracyclohexa-2,5-diene (**1**),[4] using potassium in dimethoxyethane (Scheme 1), two different paramagnetic species, (**2**) and (**3**), are detected by e s r spectroscopy The e s r spectrum[5] of the rather unstable radical anion (**2**) exhibits a large ^{19}F triplet (a_F 1 65 mT) and a partly resolved methyl proton multiplet The ion is isoelectronic with the duroquinone radical anion [6]

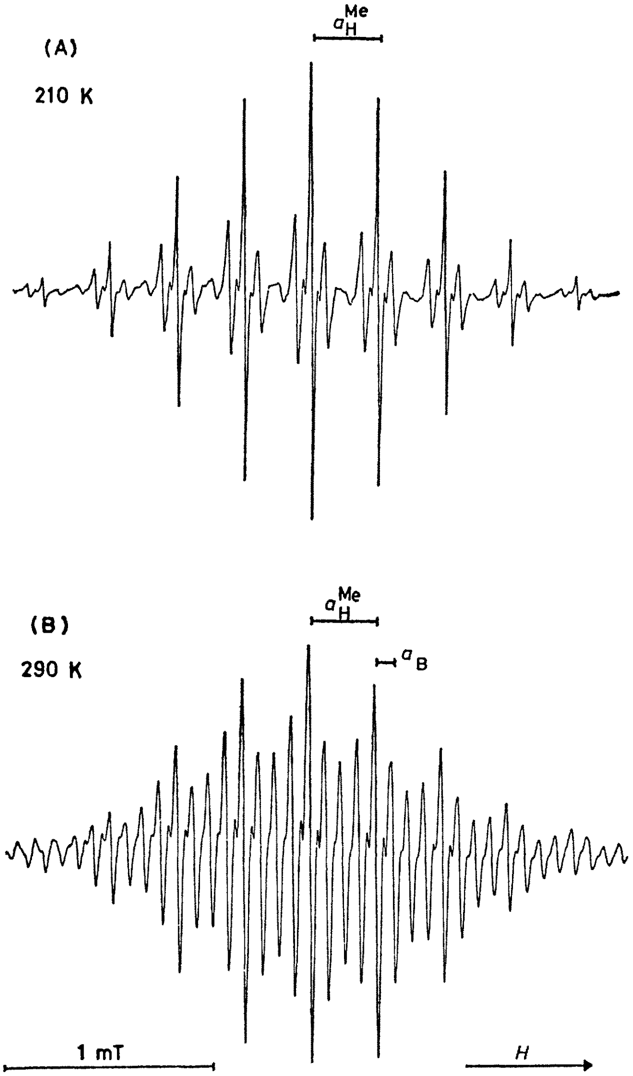
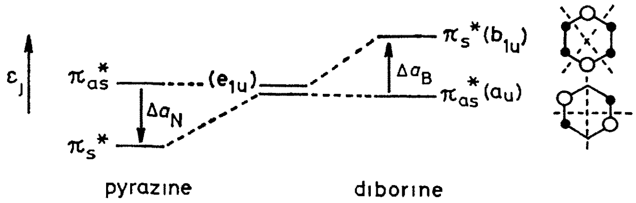


FIGURE Central part of the e s r spectrum of the 2 3 5 6-tetramethyl-1,4-diborine radical anion (**3**) at 210 K (A) and 290 K (B) Lowering of the temperature causes a broadening of all hyperfine structure lines with $M_B \neq 0$ (ref 7), leading to the dominance of the methyl proton multiplet (A) The spectrum (B) is in good agreement with a computer simulation (ref 5)

The e s r spectrum (Figure) of a secondary radical anion is observed at higher temperatures, even up to 40 °C, after the stability of the reduced system has been increased by complexing K^+ with dicyclohexano-18-crown-6 It is assigned to the radical anion of the novel heterocycle 2,3,5,6-tetramethyl-1,4-diborine (**3**), by the following arguments First, the only coupling detectable in addition to that of the 12 methyl protons is due to ^{11}B (I 3/2), *i e* there is no ^{19}F splitting Second, the spectrum correlates with that for the tetramethylpyrazine radical anion of the same symmetry[8] allowing for significant changes in the relative magnitude of the couplings The methyl proton coupling for (**3**) is almost twice as large as that for the pyrazine (a_H^{Me} 0 173 mT[8]), whereas the small[9] ^{11}B coupling in (**3**) contrasts with the large ^{14}N coupling (a_N 0 618 mT[8]) for the pyrazine The increase in π_{CC} spin density on N→B exchange can be rationalized by first-order perturbation The higher coulomb potential $\alpha_N > \alpha_C$ lowers and the smaller coulomb potential $\alpha_B < \alpha_C$ raises the benzene orbital $\pi_s^*(b_{1u})$ (Scheme 2) [2] If the radical anion spin density is represented by a singly occupied orbital $\pi_{as}^*(a_u)$, as in (**3**), then one expects large ^{1}H and almost zero ^{11}B coupling, as is actually determined by e s r spectroscopy



SCHEME 2

Neutral borabenzenes have not yet been observed although B-substituted anions $[H_5C_5BR]^-$,[10] as well as their transition metal complexes,[11] are known The stabilization of 1,4-diborine derivatives by one-electron acquisition, therefore, opens a pathway to these unstable compounds

(*Received*, *3rd March* 1980, *Com* 234)

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[1] For Part 39 of the series 'Radical Ions,' see H Bock, B Roth, and G Maier, *Angew Chem , Int Ed Engl* 1980, **19**, 147 For a comprehensive summary of e s r results from the Frankfurt PES Group see 'Computational Methods in Chemistry,' Plenum Press, New York, 1980

[2] See E Heilbronner and H Bock, 'The HMO Model and its Application,' Vol I, Wiley Interscience, London, 1976

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