Journal of Organometallic Chemistry, 234 (1982) C17—C19
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE RADICAL ANION FROM TETRA-t-BUTYLTETRABORANE(4), A NEW ROUTE TO t-Bu_4B_4

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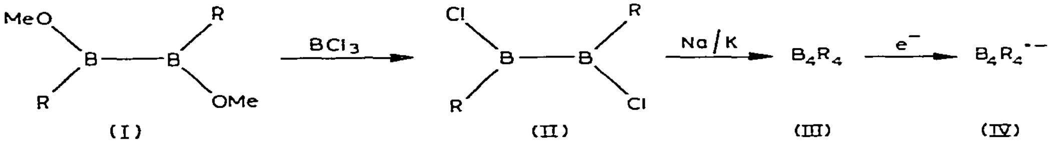
(Received May 11th, 1982)

Summary

The radical anion from tetra-t-butyltetraborane(4) has been generated from di-t-butyldichlorodiborane(4) (II) and Na/K alloy and identified by ESR spectroscopy. Formation of t-Bu_4B_4 by reductive dimerization of II is also established by ^{11}B NMR spectroscopy.

Tetra-t-butyltetraborane(4) (III) has been synthesized recently [1] from t-butyllithium and the not easily accessible B_4Cl_4 [2]. Our recent success in forming boron—boron bonds by reductive dimerization of di-t-butylhalogenoboranes [3] prompted us to check, whether di-t-butyldichlorodiborane(4) (II) [4] which is easily obtained from di-t-butyldimethoxydiborane(4) (I) [5], might be used as a precursor for the generation of III and its radical anion IV.



(a R = $C(CH_3)_3$; b R = $C(CD_3)_3$)

On reaction of IIa with Na/K alloy in THF or triglyme at room temperature we obtained the ESR spectrum shown in Fig. 1. The ESR spectrum of the radical generated from the perdeuterated diborane(4) (IIb) (Fig. 2) clearly shows a 13 line multiplet characteristic of four equivalent boron atoms. This spectrum can be simulated with $a(^{11}B)$ 1.17 G and $a(^{10}B)$ 0.39 G taking into account the isotopic species $^{11}B_4$ (43.41%) and $^{11}B_3$-^{10}B (40.28%). The spectrum of Fig. 1 can be simulated with a(H) 0.31 G for 36 equivalent protons and $a(^{11}B)$ 1.20 G (4B). We therefore conclude that the new radical, which can be

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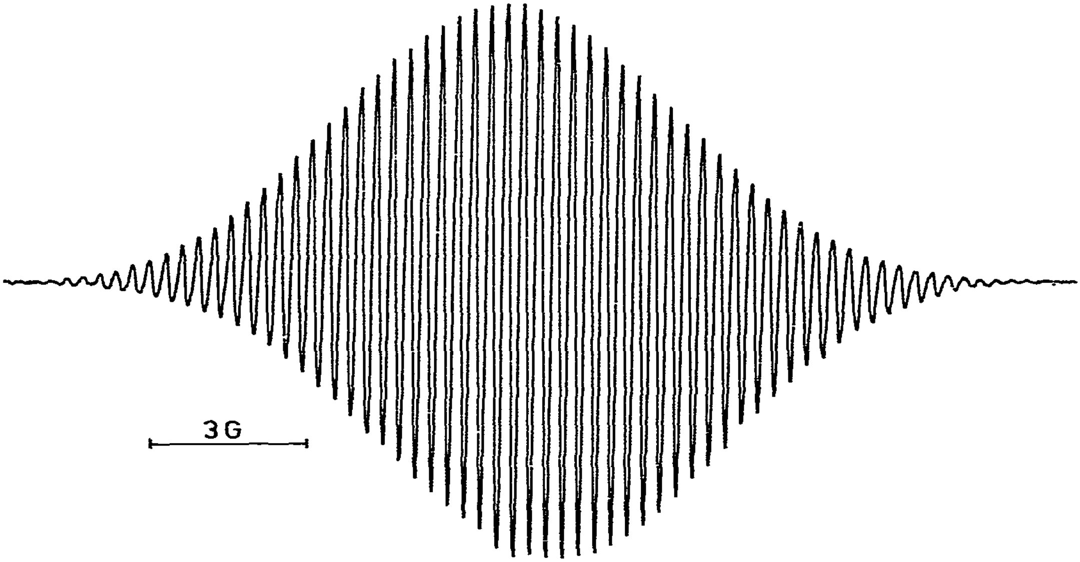


Fig. 1. ESR spectrum of the radical obtained from IIa and Na/K in THF at 80°C.

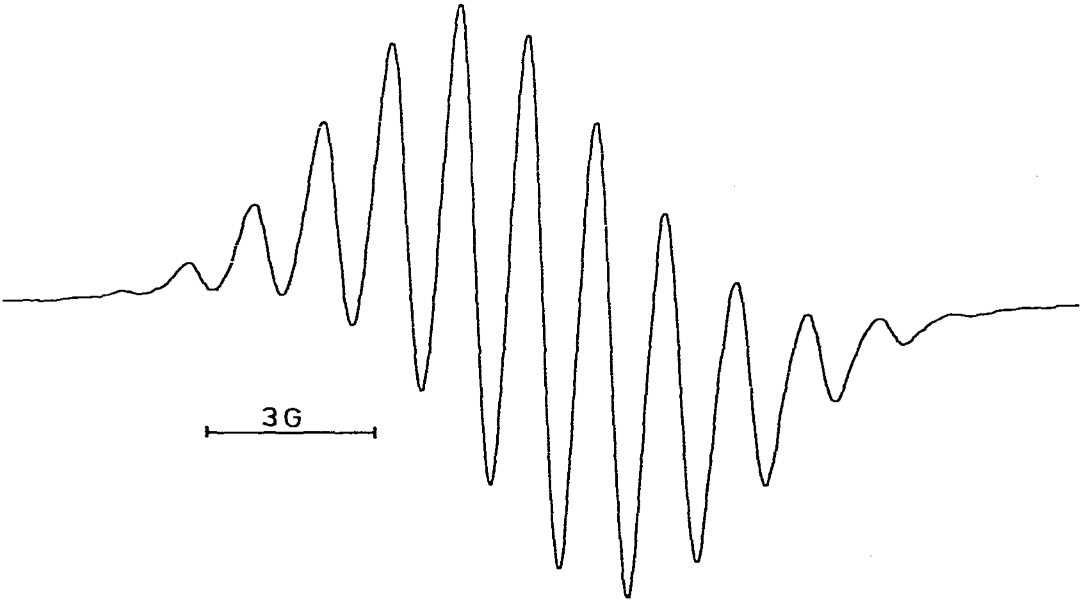
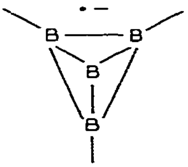


Fig. 2. ESR spectrum of the radical obtained from IIb and Na/K in triglyme at 100°C.

observed up to 230°C ($t_{1/2}$ ~ 30 min), is the radical anion IV from tetra-t-butyltetraborane(4) (III). Formation of III from II is supported by an ^{11}B NMR signal at 135.7 ppm (lit. [1] 135.1 ppm; from BF_3—OEt_2) in the reaction mixture for a preparative scale reduction of II.

The geometry of III is not known [1]. For IV we propose a puckered cyclotetraborane(4) structure VI with planar boron centers on the basis of its small boron coupling constant, which is in the order of magnitude found for π-radicals with boron—boron bonds [3,6]. In a planar conformation of VI there would be more steric hindrance between the vicinal t-butyl groups [7] and less steric screening of the boron atoms. For a tetrahedral cluster structure V with bent geometry at the boron centers we would expect a boron coupling constant at least twice that in the cluster radical anion $B_5H_8^{\cdot-}$ (2.52 G) [9], which has the unpaired electron spread over twice the number of boron atoms.



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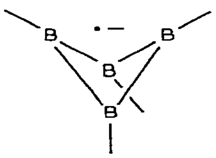

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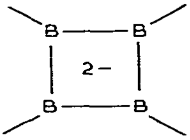
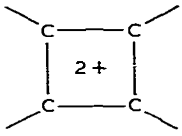


(VII)



(VIII)

Studies to transform IV into the dianion VII, which is iso-electronic with the aromatic dication VIII [10] from cyclobutadienes, are currently in progress.

Acknowledgement

We are grateful for financial support of this work by the Fonds der Chemischen Industrie.

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