

Figure 2. Laser Raman spectra (Jarrell Ash 25-300 spectrometer): (a) NaAlBu_4 in C_6H_{12} ; M = molarity in C_6H_{12} ; R = mole ratio $\text{THF}:\text{Na}^+$ (I, 0.3 M , R = 0; II, 0.25 M , R = 0; III, 0.3 M , R = 0.5; IV, 0.3 M , R = 5.0; V, 0.20 M , R = 20.0); c = cyclohexane band. (b) I, NaAlBu_4 in THF; II, KAlBu_4 in THF. Arrows indicate bands due to vibrations of the anion.

bands were observed for them. Our experiments exclude the possibility of the Raman band being due to an impurity, and we have observed it with both 632.8- (He-Ne laser) and 514.5-nm (Ar^+ ion laser) radiation. However, they do not conclusively eliminate the possibility that an inactive anion or solvent mode is being perturbed into activity or split. This is unlikely in light of the T_d selection rules for AX_4 , and selection rules for the connected n -butyl groups. A cyclohexane band at 240 cm^{-1} in both ir and Raman has been assigned⁶ to E_u (ν_{32} , ir allowed, Raman forbidden) and is found unperturbed in our spectra. Attempts to dissolve sufficient KAlBu_4 in cyclohexane at room temperature have been unsuccessful.

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(6) L. Bernard, *J. Chim. Phys.*, **63**, 772 (1966).

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A Trigonal Boron Cation

Sir:

We wish to report direct evidence concerning the existence of a boron cation, I, to our knowledge the first example of a positively charged boron species

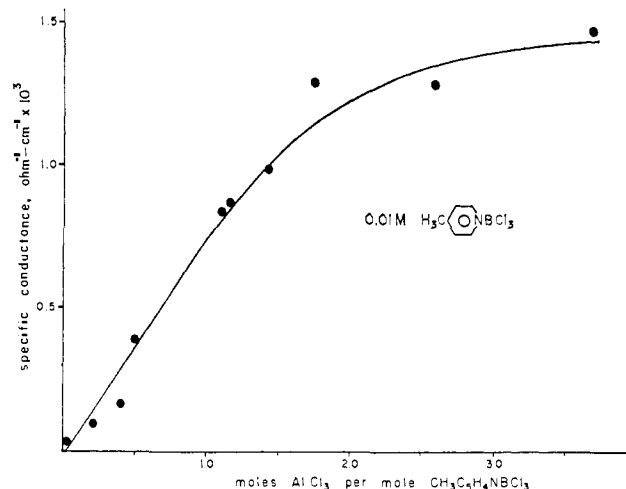
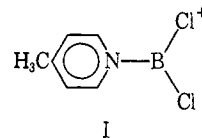


Figure 1. Conductance of $4\text{-CH}_3\text{C}_5\text{H}_4\text{NBCl}_3\text{-AlCl}_3$ in CH_2Cl_2 .

with coordination number 3 which is isoelectronic to a carbonium ion. The closest reported analog to this species, $(\text{C}_6\text{H}_5)_2\text{B}^+$ solvated with ethyl methyl ketone,¹ is apparently four-coordinate.²



Although aluminum chloride does not dissolve readily in methylene chloride, a mixture of aluminum chloride and 4-methylpyridine-trichloroborane is easily soluble. The 60-MHz proton nmr spectrum of such a solution is drastically different from one of pure 4-methylpyridine-trichloroborane in methylene chloride. The neutral borane shows a sharply defined multiplet centered at τ 0.95, which has been demonstrated to consist of a doublet of two overlapping quartets arising from spin-spin coupling of the 2,6 protons on the pyridine ring to the 3,5 ring protons and to ^{11}B in the tetrahedral environment of the coordinated BCl_3 group.³ In the presence of aluminum chloride the quartet splitting pattern completely disappears so that only the H-H doublet remains. The position of the absorption of the 2,6 hydrogens is shifted downfield relative to the tetrahedral adduct, as is the doublet arising from the 3,5 hydrogens and the singlet corresponding to the methyl substituent on the ring. The extent of this shift increases with the proportion of aluminum chloride in the sample. Representative data are given in Table I.

The collapse of the coupling pattern implies that a rapid reaction is taking place at the boron atom which decreases the symmetry of the electric field gradient at that nucleus. The concentration dependence of the chemical shifts suggest that this reaction is reversible, and the downfield direction of the shifts suggests that a positive charge is developed in the species.⁴ The simplest hypothesis explaining these data is the formation of a trigonal cation derived by reversible chloride abstraction from the neutral adduct.

(1) J. M. Davidson and C. M. French, *J. Chem. Soc.*, 114 (1958).

(2) D. R. Armstrong and P. G. Perkins, *ibid.*, A, 1026 (1966).

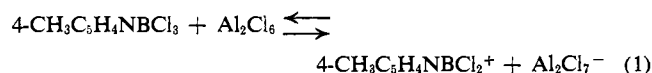
(3) G. E. Ryschkewitsch and W. J. Rademaker, *J. Magnetic Resonance*, **1**, 584 (1969).

(4) K. C. Nainan and G. E. Ryschkewitsch, *J. Amer. Chem. Soc.*, **91**, 330 (1969).

Table I. Chemical Shifts of 4-CH₃C₅H₄NBCl₃-AlCl₃ Mixtures

AlCl ₃ /4-CH ₃ - C ₅ H ₄ NBCl ₃	Chemical shift ^a		
	2,6-H	3,5-H	CH ₃
0	543	458	158
1.02	552	480	169
2.04	554	487	174
∞ ^b	559 ± 2	498 ± 4	179 ± 1

^a In Hz, at 60 MHz, relative to CH₂Cl₂ 320 Hz downfield from tetramethylsilane. ^b Extrapolated.



The ¹¹B resonance spectrum at 19.3 MHz is in agreement with this proposition. A 1:2 mixture of 4-CH₃-C₅H₄NBCl₃ and AlCl₃, which is a mobile liquid at room temperature, gives an exceedingly broad resonance 1090 ± 80 Hz wide, narrowing to 600 Hz at 57°, and centered at -29.0 ± 4 ppm relative to external B(OCH₃)₃. The ¹H or ¹¹B spectra are unchanged after heating and standing for 2 weeks. The position of the chemical shift in this mixture is important when compared to the ¹¹B shift of the neutral adduct (+10.1 ppm),⁵ a tetrahedral cation (4-CH₃-C₅H₄N)[(CH₃)₃N]BCl₂⁺ (+9.5 ppm),⁶ or BCl₃ (-28.2 ppm).⁷ Following the correlations of Nöth⁷ a large downfield shift indicates a coordination number of three for boron and is caused by a lack of shielding of the boron nucleus in a trigonal-planar configuration which is not compensated fully by internal π bonding. A shift further downfield than in BCl₃ would be expected on the basis of the net positive charge on the species,⁴ but our data are not sufficiently precise to allow this distinction to be made.

The existence of the cation is further supported by the results of conductance measurements carried out on mixtures of 4-methylpyridine-trichloroborane (0.010 M) with varying amounts of aluminum trichloride in CH₂Cl₂. The data are presented in Figure 1 and show the increase of conductance expected from the equilibrium in eq 1. The conductance at high AlCl₃ concentration approaches the value for 0.010 M (4-CH₃-C₅H₄N)[(CH₃)₃N]BCl₂⁺PF₆⁻⁶ in the same solvent, 1.493 × 10⁻³ ohm⁻¹ cm⁻¹. In comparison the solvent or 4-CH₃C₅H₄NBCl₃ is a nonconductor, whereas 0.010 M AlCl₃ gives a conductance of 0.08 × 10⁻³ ohm⁻¹ cm⁻¹ which steadily increases with time while the solution darkens. No such change is observed when excess 4-CH₃C₅H₄NBCl₃ is also present. Extrapolation of the nearly linear portion of Figure 1 to the composition 4-CH₃C₅H₄NBCl₂⁺ Al₂Cl₇⁻ gives a specific conductance of 1.5 × 10⁻³ ohm⁻¹ cm⁻¹ for a hypothetical 0.01 M solution of the salt in which eq 1 is completely displaced to the right. From the smoothed conductance curve we estimate K = 20 ± 3, for the equilibrium in eq 1 (uncorrected for nonideal behavior). Chemical shifts for the pure cation can also be extrapolated with the help of the conductance data and are listed in Table I.

(5) S. R. Eaton and W. H. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, Inc., New York, N. Y., 1969, p 474.

(6) W. J. Rademaker, Ph.D. Dissertation, University of Florida, 1969.

(7) H. Nöth and H. Vahrenkamp, *Chem. Ber.*, **99**, 1049 (1966).

The chemical behavior of the system is also in accord with our contention. Solid (CH₃)₄N⁺Cl⁻ added to a mixture of 4-CH₃C₅H₄NBCl₃ and AlCl₃ completely restores the nmr multiplet pattern of the neutral borane. Passage of excess (CH₃)₃N into the solution results in the formation of (4-CH₃C₅H₄N)[(CH₃)₃N]BCl₂⁺ which can be isolated as the PF₆⁻ salt in 30% yield after extracting the reaction mixture with water and precipitating with NH₄PF₆. The neutral adduct does not react with (CH₃)₃N in the absence of AlCl₃ under otherwise the same conditions. The trimethylamine adduct of boron trichloride appears to be considerably less reactive toward AlCl₃ since the mixture shows only a partial collapse of the long-range B-H coupling even with excess AlCl₃. This difference in behavior would be expected if the planar cation I were stabilized by the interaction of the π-electron system of the ring with an empty p orbital on boron.

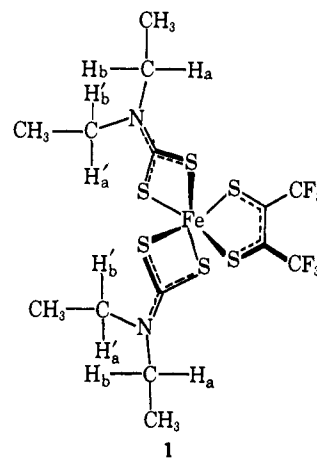
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Complexes Containing the Fe-S₆ Core with Unusual Magnetic, Electrochemical, and Stereochemical Properties

Sir:

In the course of investigating oxidative addition reactions of iron(II) with ligating sulfur compounds we have observed that bis(N,N-diethyldithiocarbamato)-iron(II),¹ Fe(Et₂-dtc)₂, and related complexes react smoothly with bis(perfluoromethyl)-1,2-dithietene² under anaerobic conditions in THF solution at 25° to afford a new series of Fe-S₆ complexes of general formulation Fe(R₂-dtc)₂[(CF₃)₂C₂S₂]. Those with R = Me, Et and R,R = (CH₂)_{4,5} are representative and have been characterized by ¹H and ¹⁹F nmr, infrared, and mass spectra, solution molecular weights, and elemental analyses. Fe(Et₂-dtc)₂[(CF₃)₂C₂S₂] (1) has been examined in the greatest detail and manifests



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(2) C. G. Krespan, *J. Amer. Chem. Soc.*, **83**, 3434 (1961).