phosphorus atom is roughly tetrahedral and replaces a bridging proton insofar as direction from the B_5 skeleton is concerned, we would recognize that one R group on phosphorus has an "axial" position well below the B_4 plane and extending toward the 4,5-B atoms, while the other R group would be "equatorial," extending outward and almost coplanar with the basal boron atoms. Then space-induction effects might be used to decide which isomer has axial CF_3 and equatorial CH_3, or *vice versa*.

By the simplest argument, a CF_3 group undergoing dipolar interaction with the especially electron-deficient 4,5-B atoms would have ^{19}F peaks more downfield and push the 4,5-B peaks upfield; and methyl groups far from the 4,5-B atoms would show relatively upfield proton peaks. All three expectations are met by the δ values for isomer A. Accordingly, there is a temptation to conclude that isomer A has axial CF_3 with equatorial CH_3 and that isomer B has the opposite situation.

However, this conclusion would lead us to expect isomer A to be stabilized by internal dipolar interaction, whereas in fact it isomerizes quantitatively to isomer B. Also, we must not forget that isomer A is associated; and the only reasonable basis for the assocation would be an intermolecular dipolar interaction between CF_3 of one molecule and the 4,5-B atoms of another. Indeed, the association may amount to more than we have demonstrated, for the 50% too-high molecular weight was determined in solution in ether, which could be expected to work against the postulated dipolar association. Attempts to determine the molecular weight in a more truly inert solvent, such as *n*-pentane, failed for lack of solubility.

Considering, then, that quite high actual molecular weights might prevail in the "neat" liquid isomer A, we may argue that this isomer could connect an equatorial CF_3 to the 4,5-B atoms of an adjacent molecule, with better space-inductive interaction (and more downfield chemical shift) than if an axial CF_3 were less effectively reaching toward 4,5-B in the same molecule. By this argument, isomer A would use equatorial CF_3 to maintain a weak dipolar polymer bonding, while axial CH_3 would be little affected by 4,5-B atoms which are receiving the charge effect of CF_3 from another molecule in a relatively effective manner. Then isomer B could be stabilized as a monomer by a dipolar action of axial CF_3 toward 4,5-B in the same molecule, while the equatorial methyl group would fail to develop effective polymer bonding to an adjacent molecule.

Both of the opposing ideas of the isomer structures have their merits, and we prefer not to choose between them at this time. Possibly the decision can be made later, on the basis of fuller information, including work on analogous compounds and more rigorously studied arguments.

Even less productive would be attempts to explain why isomer A is the exclusive product of the original synthesis.

CONTRIBUTION FROM THE AMES LABORATORY OF THE ATOMIC ENERGY COMMISSION
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The Nuclear Magnetic Resonance Spectra of Aluminum Borohydride–Trimethylamine[1a,b]

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The H^1, B^{11}, and Al^{27} nmr spectra of aluminum borohydride and its trimethylamine adduct have been examined. On the basis of these spectra and cryoscopic data, the adduct is shown to be an undissociated monomer with magnetically equivalent borons and hydridic hydrogens. The adduct is unique in that it has a lower symmetry (C_3 or C_{3v}) than the original aluminum borohydride (D_{3h}) yet the electric field gradient at the Al^{27} nucleus appears to be smaller in the adduct than in the free acceptor.

With their discovery of aluminum borohydride, Schlesinger, Sanderson, and Burg noted that it formed 1:1 adducts with trimethylamine, ammonia, and ether, all of which had some stability at room temperature.[2] Further addition of trimethylamine to its adduct resulted in the cleavage of the aluminum–boron framework to produce $(CH_3)_3NBH_3$. More recently, it has been reported that a total of 4 equiv of amine will react with aluminum borohydride to degrade it to adducts of

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[1] (a) Presented, in part, to the 74th Meeting of the Iowa Academy of Sciences, April 13, 1962, and, in part, at the 4th Omnibus Conference on Electronic and Nuclear Spectra, March 2, 1963, Pittsburgh, Pa. (b) Abstracted in part from a thesis submitted by O. V. Ziebarth in partial fulfillment of the requirements for the degree of Master of Science, Iowa State University, 1962, and in part from a thesis submitted by R. C. Hopkins in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Harvard University, 1964. (c) Alfred P. Sloan Fellow. (d) Author to whom correspondence should be addressed: Monsanto Co., Inorganic Chemicals Division, St. Louis, Mo.

[2] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Am. Chem. Soc.*, **62**, 3421 (1940).

AlH_3 and BH_3.[3] However, experimental details of the determination of this stoichiometry are not given and thus the reason for not observing the anticipated 5:1 ratio for the over-all reaction is not apparent.[4]

$$Al(BH_4)_3 + 5N(CH_3)_3 = [(CH_3)_3N]_2AlH_3 + 3(CH_3)_3NBH_3$$

Nevertheless, the complete degradation of $Al(BH_4)_3$ into AlH_3 and BH_3 units was established. A later communication reports the initial results of a room-temperature crystallographic study of $(CH_3)_3NAl(BH_4)_3$.[5] The heavy-atom skeleton has nearly tetrahedral symmetry around both the nitrogen and the aluminum. There is a direct aluminum–nitrogen bond, which is 2.01 Å in length. This can be compared with the much longer value of 2.19 Å in $[(CH_3)_3N]_2AlH_3$.[6] There is also a low-temperature form with similar bond lengths in which the tetrahedral symmetry about the aluminum has been lost.[7] The bond lengths suggest that $Al(BH_4)_3$ is a much stronger Lewis acid than $(CH_3)_3NAlH_3$. The infrared spectrum of $(CH_3)_3NAl(BH_4)_3$ has been reported in part and a few assignments have been made.[3,8] A complete infrared and Raman spectral study using isotopically substituted aluminum borohydrides is in progress and will be reported later.[9] Proton and B^{11} nuclear magnetic resonance spectra have been reported for $Al(BH_4)_3N(CH_3)_3$[3,8] but no Al^{27} spectrum. Since the structure in solution may well be different from that in the solid state, we wish to report our results and conclusions, based primarily on nuclear magnetic resonance data.

Results and Discussion

The H^1, Al^{27}, and B^{11} nuclear magnetic resonance results are given in Figures 1–4. Where available, the chemical shifts and coupling constants agree well with the value reported by other authors.[3,7] A cryoscopic molecular weight of 113.5 was determined in benzene at 0.012 and 0.007 *F*. This compares reasonably well with 130.6 calculated for a monomer with no dissociation into ligand and acceptor or association to form higher aggregates. An Al^{27} spectrum of a solution of 3 parts of $Al(BH_4)_3$ and 2 parts of $N(CH_3)_3$ shows two separate and distinct peaks, while that of pure $(CH_3)_3NAl(BH_4)_3$ in benzene shows a single multiplet. Thus it would seem that any dissociation of the complex is negligible and intermolecular trimethylamine exchange is slow. Bird and Wallbridge also found a monomeric behavior cryoscopically.[3]

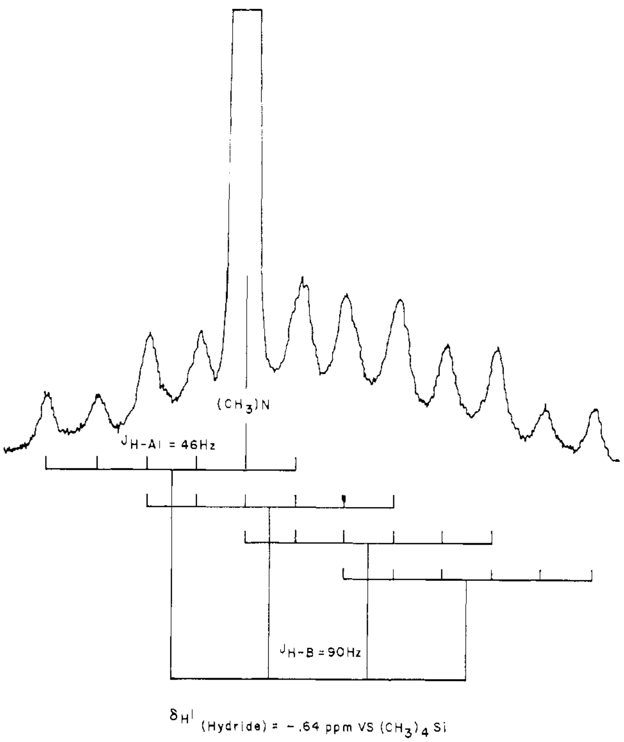

Figure 1.—Proton magnetic resonance spectrum of $(CH_3)_3NAl(BH_4)_3$ in benzene at 60 Mc.

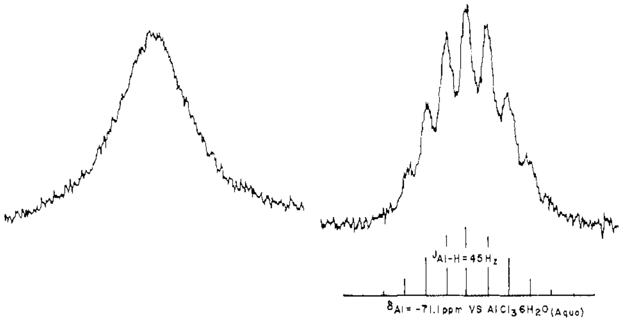

Figure 2.—Al^{27} nmr (8.5-Mc) spectra of $Al(BH_4)_3$ and $(CH_3)_3NAl(BH_4)_3$ in benzene.

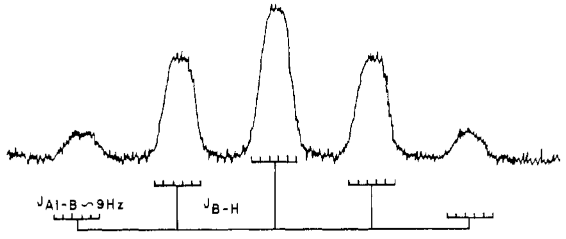

Figure 3.—B^{11} nmr spectrum of $(CH_3)_3NAl(BH_4)_3$ in benzene at 15.1 Mc.

The nuclear magnetic resonance data contain several interesting results. First of all, the proton spectrum shows a 12-fold multiplet plus the N-methyl peak as shown in Figure 1 and as reported previously.[3] By comparison, $Al(BH_4)_3$ shows only a broad, unresolved peak at room temperature.[10,11] The constant spacing of this multiplet at 60 and 40 MHz identifies its source as spin–spin coupling and proves the equivalence of all 12 hydridic protons. The pattern of overlapping peaks shown in Figure 1 is the result of the coupling of each proton to one of the three spin-$^3/_2$ B^{11} nuclei and to the spin-$^5/_2$ Al^{27} nucleus.

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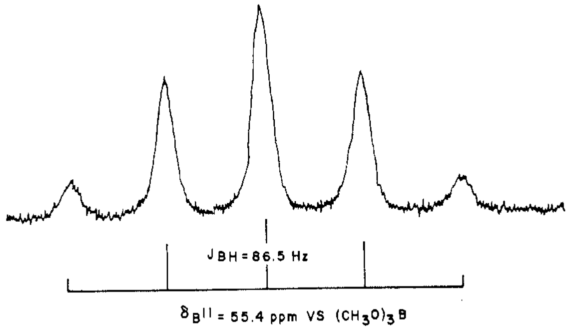

Figure 4.—B^{11} nmr spectrum of $(CH_3)_3NAl(BH_4)_3$ in benzene at 15.1 Mc with Al^{27} decoupling.

The pattern from the 18.8% abundant spin-3 B^{10} is not resolved. Such a spectrum requires the rapid interchange of the four hydrogens within each BH_4 group. Moreover, the time of association of any given hydrogen with any given boron or aluminum must be long. Thus, any exchange of either hydrogen, BH_4 ions, or BH_3 groups between molecules is ruled out or is, at most, very slow compared to the Al–H or B–H coupling constants. Although proton tunneling has been suggested as a mechanism for the corresponding process in $Al(BH_4)_3$,[10,11] any mechanism that is entirely intramolecular is consistent with the observation of proton–aluminum coupling. The most curious feature of the spectrum is the long Al^{27} relaxation time, implying a smaller electric field gradient at the aluminum in the trimethylamine adduct than in the free aluminum borohydride. In the latter compound, the coupling is partially or completely averaged out by Al^{27} relaxation. In this connection, it is interesting to note that of the six complexes of the type $L\cdot Al(BH_4)_3$ reported by Bird and Wallbridge, where L was $(CH_3)_3N$, $(CH_3)_3P$, $(CH_3)_3As$, $(CH_3)_2O$, $(C_2H_5)_2O$, or $(CH_3)_2S$, only the amine complex showed coupling of the hydrides to the aluminum.

Pople has discussed the relationship between proton line widths and the quadrupole transition probabilities for the various states of a high-spin nucleus coupled to a proton.[12] This relationship predicts that the relative line widths of an Al^{27} sextet in a proton spectrum should be 45:69:54:54:69:45. Because of the superposition of the sextets only the ratio of the $^3/_2$ to the $^5/_2$ lines can be compared. We observe a ratio of 0.69 for the heights of these peaks as compared to a theoretical value of 0.65.

Seven peaks are clearly resolved in the Al spectrum of the adduct in Figure 2. The relative intensities 25, 55, 87, 100, 91, 60, 31 fit the pattern expected for a 13-line multiplet of 0.1, 1.3, 7, 24, 54, 86, 100, 86, etc., confirming the conclusion from the proton spectrum that the Al^{27} nucleus is coupled to 12 equivalent nuclei of spin $^1/_2$.

The B^{11} spectrum in Figure 3 is the anticipated quintet of the proper intensities for a borohydride ion. Thus, the lifetime of association of a hydrogen with a boron is also long with respect to the time for interchange within a BH_4 unit. Not only is the exchange intramolecular but the association between a given proton and boron persists throughout the exchange.

A striking feature of the boron spectrum is the flat tops of the peaks. Double irradiation to decouple the Al^{27} nucleus narrows the lines markedly as shown in Figure 4, conclusively proving that Al–B coupling is responsible for most of the width of the peaks. Although this coupling is unresolved an approximate coupling constant of 9.5 Hz can be estimated.

The similarity between the nuclear magnetic resonance spectra of $Al(BH_4)_3$ and its $N(CH_3)_3$ adduct is most striking. The chemical shifts observed for $Al(BH_4)_3$ are: H, 1.5 ppm; B, 55.2 ppm; and Al, 97.4 ppm, all relative to the same standards used for the adduct. The coupling constants for the uncomplexed borohydride are $J_{BH} = 89$ Hz and $J_{H-Al} = 4.4$ Hz.[10] By comparison with the values given in the figures for the adduct it will be noted that, except for the chemical shift of the aluminum, all values are essentially the same for both the adduct and the uncomplexed acceptor. It is to be anticipated that the environment of the aluminum atom would be affected most profoundly. However, the groups attached to an acceptor atom usually experience a measurable shift in shielding constant upon complex formation.[13,14]

Experimental Section

Materials were prepared by standard high-vacuum techniques[2,15] and were handled either under vacuum or under rigorously dried nitrogen. The various nmr instruments used were the commercially available Varian models operated at the appropriate field strengths and frequencies for each nucleus. The double-resonance instrument used for the decoupling experiments has been described.[16] Proton chemical shifts were measured relative to internal benzene as a secondary standard. The chemical shift of benzene relative to $(CH_3)_4Si$ was assumed to be -7.07 ppm. Chemical shifts for B^{11} were measured relative to external triethyl borate, used as a secondary standard and assumed to have a shift of 0.6 ppm relative to trimethyl borate, the primary standard.[17] Chemical shifts for Al^{27} were measured relative to external saturated $AlCl_3\cdot 6H_2O$.

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