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cyclo-1,5-Bis-μ-dimethylamino-3,7-di-μ-hydrido-2,4,6,8-tetrakis(dimethylaluminum)

BY J. D. GLORE,[1] R. E. HALL,[1] AND E. P. SCHRAM*

Recieved June 17, 1971

Treatment of $[Al(CH_3)_3]_2$ with $[(CH_3)_2NBH_2]_2$ affords $[(CH_3)_2NAl(CH_3)_2]_2$, $[(CH_3)_2AlH]_3$, $B(CH_3)_3$, and $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$. This last species crystallizes in the space group $P2_1/n$ $[\pm(x, y, z), \pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)]$ with a = 14.177 (0.009), b = 10.371 (0.007), c = 7.693 (0.005) Å, and cos β = −0.0129 (0.0004)°; ρ_{calcd} = 0.934 g/cm³ for mol wt 318.37 and Z = 2. The structure involves an eight-membered ring containing 4 Al, 2 N, and 2 H. A possible mechanism of formation for $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ is discussed as well as infrared assignments associated with this new species.

Introduction

In order to understand the reaction between $[Al(CH_3)_3]_2$ and $B_3Al_3[N(CH_3)_2]_7H_5$, the reactions of $[Al(CH_3)_3]_2$ with $[(CH_3)_2N]_2BH$ and $[(CH_3)_2NBH_2]_2$ have been investigated. The $[(CH_3)_2N]_2BH$ reaction has been reported;[2] the reaction with $[(CH_3)_2NBH_2]_2$ is the subject of this investigation.

Results and Discussion

Treatment of dimethylaminoborane, $[(CH_3)_2NBH_2]_2$, with excess aluminum trimethyl, $[Al(CH_3)_3]_2$, at 80° affords dimethylaminodimethylaluminum, $[(CH_3)_2NAl(CH_3)_2]_2$, dimethylalane, $[(CH_3)_2AlH]_3$, boron trimethyl, $B(CH_3)_3$, and *cyclo*-1,5-bis-μ-dimethylamino-3,7-di-μ-hydrido-2,4,6,8-tetrakis(dimethylaluminum), $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$. Because $[(CH_3)_2NAl(CH_3)_2]_2$ and $[(CH_3)_2AlH]_3$ have similar volatilities, it was not possible to effect complete species separation; however each of the cited compounds was positively identified as a reaction product. It was not possible to obtain an estimate of the relative amounts of the various products by ¹H nmr because of rapid exchange in solution. Comparative infrared spectroscopy indicated all the cited species are major products. Treatment of $[(CH_3)_2NBH_2]_2$ with $[Al(CH_3)_3]_2$ at 80° is believed to be best described by

$$6[Al(CH_3)_3]_2 + 2[(CH_3)_2NBH_2]_2 \longrightarrow Al_4(CH_3)_8[N(CH_3)_2]_2H_2 + [(CH_3)_2NAl(CH_3)_2]_2 + 2[(CH_3)_2AlH]_3 + 4B(CH_3)_3 \quad (1)$$

The analytical characterization of $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ (I) is summarized in Table I and the molecular formulation is established by a single-crystal X-ray structure study. An X-ray diffraction study was necessary to establish the molecular formulation of I because ¹H nmr and mass spectral data indicated rapid decomposition in solution and in the gas phase. The specific modes of decomposition for I in solution and in the gas phase will be reported shortly.

TABLE I

ANALYTICAL DATA FOR $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$

% Al		% $N(CH_3)_2$		% CH_3 (hydrolyzable)		% H (hydrolyzable)	
Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
34.0	34.7	27.7	27.1	37.7	37.6	0.63	0.61

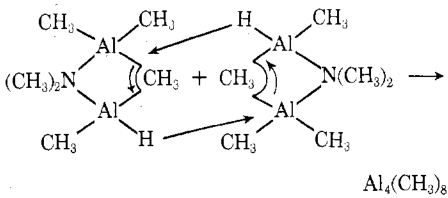
Structure of I.—The molecular geometry of $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ consists of an eight-membered ring with the ring structure consisting of the alternating atoms $\underline{\text{Al–H–Al–N–Al–H–Al–N}}$. Two terminal CH_3 moieties are associated with each Al and N atom. The 4 Al and 2 H atoms all lie in the same plane within ±0.1 Å while one N moiety is above this plane and the other below. The refined crystallographic data (R < 4.6%) associated with I will be reported shortly.[3]

Possible Mechanism of Formation of I.—The instability of I in solution is thought to be a consequence of rapid exchange affording the more stable product species as indicated by

$$Al_4(CH_3)_8[N(CH_3)_2]_2H_2 \longrightarrow [(CH_3)_2NAl(CH_3)_2]_2 + {}^2/_3[(CH_3)_2AlH]_3 \quad (2)$$

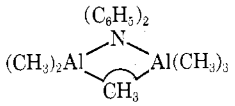
The reaction represented by eq 2 takes place spontaneously in solution but is an idealized representation of this chemical system because small quantities of exchange products have been inferred by ¹H nmr studies. The fact that I is an unstable species in solution, eq 2, and represents the first example of a hydride-bridged aluminum heterocycle which is completely characterized prompts us to speculate on the mechanism of its formation. The suggested intermediates have been extremely useful in our approach to developing the chemistry $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$.

Compound I may be thought of as a dimer of $(CH_3)_2AlH \cdot (CH_3)_2NAl(CH_3)_2$ with single or mixed bridged ligands—CH_3, $N(CH_3)_2$, and/or H. Because the final product, I, is formally a dimer of $(CH_3)_2AlH \cdot (CH_3)_2NAl(CH_3)_2$, the structure of this proposed intermediate is suggested to possess asymmetry and hence reactivity as represented by



$Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ (3)

Dimerization of this intermediate adduct to afford I, eq 3, is suggested to involve intermolecular hydride attack on the methyl bridge. There is precedence for such a mixed bridged intermediate species, *e.g.*, the structure of



has been established by an X-ray study.[4]

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[1] Work completed in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, Columbus, Ohio.

[2] R. E. Hall and E. P. Schram, *Inorg. Chem.*, **10**, 192 (1971).

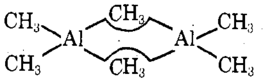
[3] P. W. R. Corfield, unpublished work.

[4] V. R. Magnuson and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 2544 (1969).

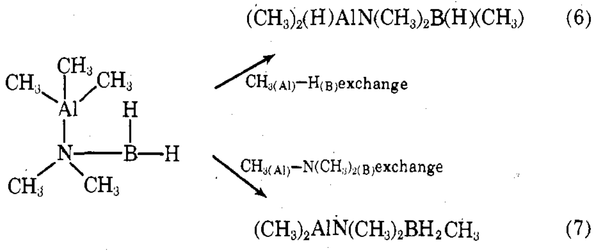
Because the components of I are the thermodynamically stable species, eq 2, the mechanism for formation of $(CH_3)_2AlH \cdot (CH_3)_2NAl(CH_3)_2$ most likely involves reaction of at least one of its monomeric component species with the other molecular component. Furthermore, because $[(CH_3)_2AlH]_3$ may be cleaved by $N(CH_3)_3$ to afford $(CH_3)_2AlH \cdot N(CH_3)_3$ while $[(CH_3)_2AlN(CH_3)_2]_2$ does not react with $N(CH_3)_3$, the reaction step prior to formation of $(CH_3)_2AlH \cdot (CH_3)_2NAl(CH_3)_2$ is suggested to involve nucleophilic attack by *in situ* monomeric $(CH_3)_2NAl(CH_3)_2$ on $[(CH_3)_2AlH]_3$, eq 4. It has been demonstrated that $[(CH_3)_2NAl(CH_3)_2]_2$ does not react with $[(CH_3)_2AlH]_3$ up to 84°; therefore the cleaving of a double-N bridge by $(CH_3)_2AlH$ is unlikely.

$$^1/_3[(CH_3)_2AlH]_3 + (CH_3)_2NAl(CH_3)_2 \longrightarrow (CH_3)_2AlH(CH_3)_2NAl(CH_3)_2 \quad (4)$$

Both reactants, $Al(CH_3)_3$ and $(CH_3)_2NBH_2$, are dimers at room temperature with the result that an elevated reaction temperature, 80°, is necessary to initiate reaction. The first reaction step is considered to be cleavage of the $[Al(CH_3)_3]_2$ methyl bridge by three-coordinate N, eq 5. The elevated reaction temperature is considered necessary to afford monomeric $N(CH_3)_2BH_2$ rather than monomeric $Al(CH_3)_3$ because $[Al(CH_3)_3]_2$ readily reacts with monomeric $(CH_3)_2NB(CH_3)_2$ to afford $[(CH_3)_2AlN(CH_3)_2]_2$ and $B(CH_3)_3$. Therefore $[Al(CH_3)_3]_2$ is known to be a reactive species toward noncoordinated $N(CH_3)_2$ moieties. The intermediate represented as product, eq 5, could rearrange by two paths



$$+ N(CH_3)_2BH_2 \longrightarrow (CH_3)_3AlN(CH_3)_2BH_2 \quad (5)$$



$$(CH_3)_2(H)AlN(CH_3)_2B(H)(CH_3) \quad (6)$$

$$(CH_3)_2AlN(CH_3)_2BH_2CH_3 \quad (7)$$

Both paths 6 and 7 are likely with subsequent elimination of the boron-containing fragment, eq 8 and 9. The boron-containing product species (eq 8, 9) are known to react with $[Al(CH_3)_3]_2$; hence the excess $[Al(CH_3)_3]_2$, present in the reaction system, would be expected to afford $B(CH_3)_3$, $[(CH_3)_2NAl(CH_3)_2]_2$, and $[(CH_3)_2AlH]_3$. Therefore the by-products associated with formation of I are readily explained.

$$(CH_3)_2(H)AlN(CH_3)_2B(H)(CH_3) \longrightarrow {}^1/_3[(CH_3)_2AlH]_3 + (CH_3)_2NB(H)CH_3 \quad (8)$$

$$(CH_3)_2AlN(CH_3)_2BH_2(CH_3) \longrightarrow (CH_3)_2AlN(CH_3)_2 + {}^1/_2[BH_2(CH_3)]_2 \quad (9)$$

Infrared Assignments.—A considerable effort has been made toward ir assignments for $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$, by correlative methods, in the hope that group frequency tabulations will aid others in the characterization of subsequent organoaluminum species. In the past, only a few such studies have been carried out on well-characterized (structurally) organoaluminum compounds.

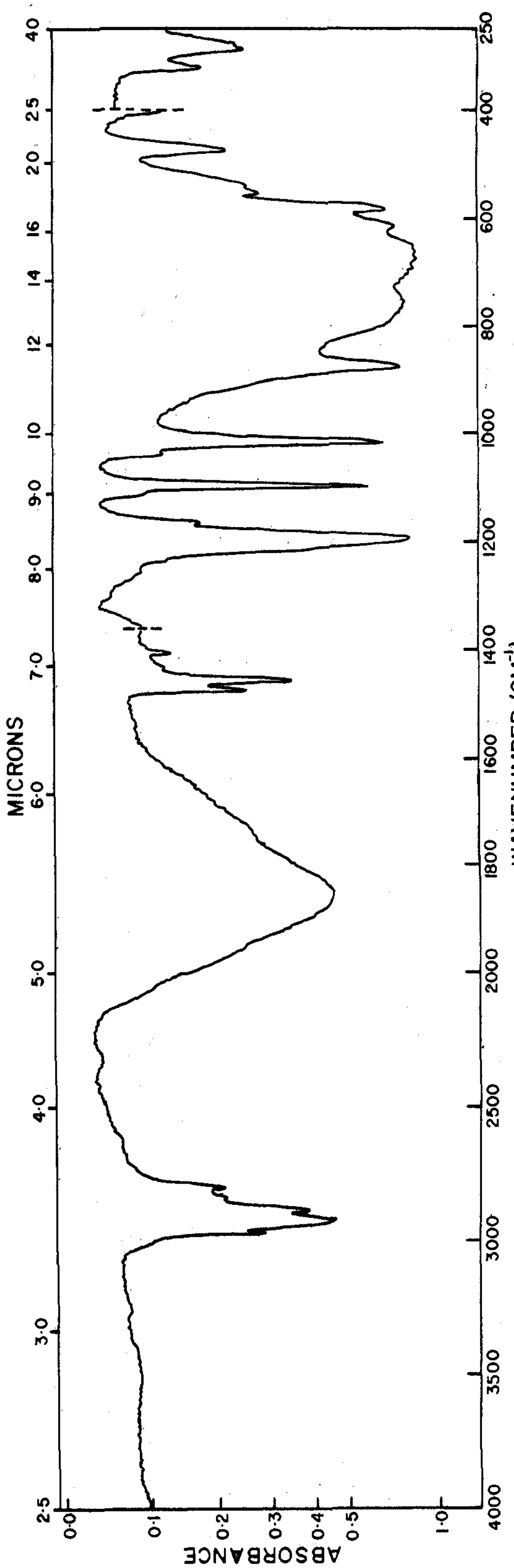


Figure 1.—Infrared spectrum of $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$.

The infrared spectrum of I is shown in Figure 1 and

TABLE II

INFRARED FREQUENCIES (CM^{-1}) AND TENTATIVE ASSIGNMENTS FOR $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$[a]

Freq ±5 cm^{-1}	Tentative assignment	Freq ±5 cm^{-1}	Tentative assignment
2970 s		876 vs	δ(Al–H)
2923 vs			
2882 vs	ν(C–H)	775 vs, b	$\nu_{as}(AlC_2)$
2838 m			
2799 m		670 vs, b	$\delta(CH_{3(Al)})$
1860 vs, b	ν(Al–H)	618 vs	$\delta(CH_{3(Al)})$
1475 s		581 vs	$\nu_s(AlC_2)$
1456 vs	$\delta(CH_3)$		
1404 w		553 m	$\nu_{as}(NAl_2)$
1212 sh		539 m	$\nu_s(NAl_2)$
1194 vs	$\rho(CH_3)$		
1165		474 m	$\delta(CH_{3(Al)})$
1098 vs	$\nu_{as}(NC_2)$	321 m	?
1018 vs	$\nu_s(NC_2$ bridge)	288 s	?

[a] Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad.

summarized in Table II. The indicated assignments are suggested as a consequence of comparing the spectrum of I with those of $[(CH_3)_2AlN(CH_3)_2]_2$, $[(CH_3)_3Al]_2$, $[(CH_3)_2AlH]_3$, and $\{[(CH_3)_2N]_3Al\}_2$.[5] In addition several reassignments of group vibrations are suggested which appear to be inconsistent as indicated in the following discussion.

In general, the infrared vibrations of aminomethylalanes may be divided into the following regions: ν(CH) (3000–2800 cm^{-1}), ν(AlH) (1600–2200 cm^{-1}), $\delta(CH_3)$ (1400–1500 cm^{-1}), $\rho(CH_3)$ (1150–1250 cm^{-1}), $\nu(NC_2)$ (1100–900 cm^{-1}), terminal and bridging N, δ(AlH) (940–840 cm^{-1}?), methyl deformation associated with (1) terminal and bridge CH_3–Al and (2) bridging and terminal dimethylamino moieties (nitrogen bridged) (*ca.* 800–575 cm^{-1}), ν(AlN) (550–500 cm^{-1}), bridge methyl deformation (*ca.* 480 cm^{-1}).

Concerning the infrared spectrum of I, the CH assignment (Table II) above 1100 cm^{-1} requires no discussion. The broad band centered at 1860 cm^{-1} is unequivocally assigned to ν(AlH) and the extreme breadth of the absorption is consistent with bridging rather than terminal AlH. The nitrogen-bridged NC_2 vibrations $\nu_{as}(NC_2)$ (1098 cm^{-1}) and $\nu_s(NC_2)$ (1018 cm^{-1}) are assigned with respect to $[(CH_3)_2AlN(CH_3)_2]_2$ (1049 and 918 cm^{-1}), respectively. Concerning the bridging δ(AlH), Hoffman has assigned the bands observed in $[(CH_3)_2AlH]_3$ at 760 and 940 cm^{-1} to different deformation modes.[6] The assignment at 940 cm^{-1} appears questionable because it is based on a comparison of noncoincident polarizable Raman absorptions with weak infrared bands. The assignment of 760 cm^{-1} may be correct; however, this region of the ir spectrum is extremely rich due to CH_3Al deformation. Hoffman was not able to characterize the strong absorption he found centered at 850 cm^{-1} in $[(CH_3)_2AlH]_3$. When one compares the infrared spectra of the five previously cited compounds, only $[(CH_3)_2AlH]_3$ and I have strong sharp bands from 875 to 850 cm^{-1}—for this reason the absorption at 876 cm^{-1} is tentatively assigned to δ(AlH). The specific absorptions, Table II, in the region 800–575 cm^{-1} are to be considered tentative because specific assignments are most difficult; however, these assignments are consistent with the cited literature assignments. Assignments are not made for the bands at 618 and 581 cm^{-1} because the only consistent assignment involves bridging $\delta(CH_{3(Al)})$ and there are no bridging methyl groups associated with I. Assignments for the low-energy absorptions 321 and 288 cm^{-1} are not made because of lack of comparative data.

Two regions remain to be assigned, 474 and *ca.* 540–550 cm^{-1}. Hoffman[6] has assigned the band observed at 480 cm^{-1} in $[(CH_3)_3Al]_2$ to a bridging $\delta(CH_3Al)$ mode—of the compounds under discussion both $[(CH_3)_2AlN(CH_3)_2]_2$ and I also exhibit such absorptions at 476 and 474 cm^{-1}, respectively. For this reason the 476-cm^{-1} band is assigned to terminal $\delta(CH_3Al)$. The absorptions found at 553 and 539 cm^{-1} are assigned to $\nu_{as}(NAl_2)$ and $\nu_s(NAl_2)$, respectively, by comparison with the assignment for $[(CH_3)_2AlN(CH_3)_2]_2$ ($\nu(NAl_2)$ 509 cm^{-1}), $\{[(CH_3)_2N]_3Al\}_2$ ($\nu_{as}(NAl_2)$ 546 cm^{-1} and $\nu_s(NAl_2)$ 524 cm^{-1}).

The chemistry of I is currently under development. Its reaction (1) with $O(CH_3)_2$ affords CH_4 (as does $[(CH_3)_2AlH]_3$), (2) with $N(CH_3)_3$ affords either $(CH_3)_2AlHN(CH_3)_3$ and $[(CH_3)_2NAl(CH_3)_2]_2$ or $(CH_3)_2AlHN(CH_3)_3$ and $Al_3(CH_3)_6[N(CH_3)_2]_2H$, depending on specific reaction conditions, (3) with C_2H_4 forms both H-insertion and π complexes, and (4) with B_2H_6 affords a borohydride derivative. The details of these chemical transformations will be reported shortly.

Experimental Section

Apparatus and Procedures.—Equipment, techniques, and analytical methods employed have been previously described.[5] Infrared data were recorded from Nujol and Fluorolube mulls prepared in a drybox employing Na–K alloy as the drying–deoxygenating agent. Both mulling agents were dried with Linde 5A Molecular Sieves.

Reagents.—Dimethylaminoborane, $[(CH_3)_2NBH_2]_2$, prepared by the literature method, had a vapor tension of 9.5 Torr at 23.0° after sublimation; lit. value 9.1 Torr at 23.0°.[7] Trimethylaluminum, $[Al(CH_3)_3]_2$, obtained from the Ethyl Corp., was fractionated through a trap at −22.9° into a −45.2° trap. The material retained at −45.2° had a vapor tension of 8.9 Torr at 20°; lit. value 8.8 Torr.[8]

Preparation of $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$.—Trimethylaluminum, $Al(CH_3)_3$ (20 mmol), was condensed onto dimethylaminoborane, *ca.* 5 mmol of $H_2BN(CH_3)_2$, and the mixture was stirred for 24 hr at 80°. The materials which were volatile at −78°, were perodically removed. Boron trimethyl, *ca.* 4 mmol, was removed from the reaction mixture maintained at −78° and characterized by its vapor tension at −78° (29 Torr[8]) and its infrared spectrum. The materials volatile at 25° consisted of $[(CH_3)_2AlN(CH_3)_2]_2$, $[(CH_3)_2AlH]_2$, and excess $[(CH_3)_3Al]_2$. The infrared spectrum of the $[(CH_3)_2AlN(CH_3)_2]_2$ was identical with that of an authentic sample, and the ^1H nmr spectrum consists of two singlets at −2.06 and +0.56 ppm from TMS in a 1:1 area ratio; these same values were obtained for an authentic sample. The infrared spectrum[6] and vapor tension of the $[(CH_3)_2AlH]_3$ agreed with those of a known sample (1.8 Torr at 24.7°); the excess $[Al(CH_3)_3]_2$ was identified by its infrared spectrum.[5]

Purification and Characterization of $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$.—This white solid was sublimed at 50–60° to a cold-water condenser with continual pumping to remove traces of $[(CH_3)_2AlN(CH_3)_2]_2$ and $[(CH_3)_2AlH]_3$. The sublimed crystals melt sharply, 97–98°, but decompose with repeated meltings as indicated by subsequently lower melting points and longer melting point ranges. The original white solid is soluble in pentane and benzene but with rapid decomposition as evidenced by the formation of new ^1H nmr absorptions within 15 min.

A 41.6-mg sample of this white solid reacts very exothermically with H_2O to afford 0.251 mmol of hydrogen and 1.036 mmol of methane. This noncondensable gaseous mixture was char-

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(5) R. E. Hall and E. P. Schram, *Inorg. Chem.*, **8**, 270 (1969).

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(7) A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, **71**, 3451 (1949).

(8) R. J. Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948, p 123.

acterized by combustion over CuO to water and water plus CO_2 at 300 and 800°, respectively.

Reaction of $[(CH_3)_2AlH]_3$ with $[(CH_3)_2NAl(CH_3)_2]$.—Treatment of $[(CH_3)_2AlNR_2]_2$, 1.46 mmol, with $[(CH_3)_2AlH]_3$, 1.95 mmol, was effected in a sealed ampoule at various temperatures from 25 to 84°. Subsequent separations of the reaction mixtures *via* fractional condensation afforded only starting materials as characterized by those infrared spectra.

Preliminary X-Ray Single Crystal Study.—A crystal of sublimed $Al_4(CH_3)_8[N(CH_3)_2]_2H_2$ was mounted in a 0.5-mm X-ray capillary tube and sealed under a nitrogen atmosphere. The space group $P2_1/n$ was determined by the systematic absences $k = 2n + 1$ for $0k0$ and $h + 1 = 2n + 1$ for $h01$ observed in two zero-level and two first-level precession photographs. The crystal was then mounted on a Picker four-circle X-ray diffraction apparatus and 18 reflections were located. A least-squares refinement of these 18 data points gave cell dimensions $a = 14.177\ (0.009)$, $b = 10.371\ (0.007)$, $c = 7.693\ (0.005)$ Å, and cos $\beta = -0.0129\ (0.0004)°$. The density calculated from these dimensions, a molecular weight of 318.37, and $Z = 2$ is 0.934 g/cm^3. The experimental density could not be determined due to the reactive nature of this substance. Collection of data and solution of the structure will be published at a later date.

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The Microwave Spectra, Structures, and Dipole Moments of Trimethylphosphine–Borane and Methylphosphine–Borane

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The microwave spectra of four isotopic species of $(CH_3)_3P \cdot BH_3$ and nine isotopic species of $CH_3PH_2 \cdot BH_3$ have been assigned. For $(CH_3)_3P \cdot BH_3$, the following structural parameters were determined: $r(PB) = 1.901 \pm 0.007$ Å; $r(PC) = 1.819 \pm 0.010$ Å; $r(CH) = 1.08 \pm 0.02$ Å; $r(BH) = 1.212 \pm 0.010$ Å; $\angle CPC = 105.0 \pm 0.4°$; $\angle HCH = 109.3 \pm 1.0°$; $\angle HBH = 113.5 \pm 0.5°$. In deriving the structure, the methyl groups were assumed to be symmetric with a hydrogen–hydrogen distance of 1.760 Å. For $CH_3PH_2 \cdot BH_3$, the following structural parameters were determined: $r(PH) = 1.404 \pm 0.006$ Å; $r(PB) = 1.906 \pm 0.006$ Å; $r(PC) = 1.809 \pm 0.006$ Å; $r(BH_s) = 1.234 \pm 0.023$ Å; $r(BH_a) = 1.229 \pm 0.022$ Å; $r(CH_a) = 1.087 \pm 0.004$ Å; $r(CH_s) = 1.098 \pm 0.016$ Å; $\angle H_aBH_s = 116.1 \pm 0.8°$; $\angle H_aBH_a = 112.3 \pm 1.2°$; $\angle H_aCH_s = 110.4 \pm 0.6°$; $\angle H_aCH_a = 108.1 \pm 0.4°$; $\angle HPH = 99.9 \pm 0.4°$; $\angle HPC = 103.2 \pm 0.6°$; $\angle CPB = 115.7 \pm 0.4°$; $\angle HPB = 116.3 \pm 0.6°$; $\angle PBH_a = 102.9 \pm 0.6°$; $\angle PBH_s = 104.2 \pm 1.0°$; $\angle PCH_a = 108.3 \pm 0.4°$; $\angle PCH_s = 111.3 \pm 1.0°$. The BH_3 and CH_3 groups were staggered with respect to the PH bonds. Dipole moments of 4.99 ± 0.2 D for $(CH_3)_3P \cdot BH_3$ and 4.66 ± 0.05 D for $CH_3PH_2 \cdot BH_3$ were obtained from Stark splittings.

Introduction

Trimethylphosphine–borane and methylphosphine–borane are addition compounds formed by the reaction of B_2H_6 with $(CH_3)_3P$ and CH_3PH_2, respectively. Burg and Wagner first characterized the compounds.[1] They discovered that $(CH_3)_3P \cdot BH_3$ is a crystalline solid which melts at 103°, while $CH_3PH_2 \cdot BH_3$ is a liquid at room temperature. The adducts are quite stable; $(CH_3)_3P \cdot BH_3$ can be heated to about 200° before decomposing slightly, while $CH_3PH_2 \cdot BH_3$ produces H_2 and polymeric material above 80°. There was no evidence for dissociation of either adduct at room temperature.

Several structural studies have been completed for various borane adducts,[2-4] but no structural data exist for the simple methylphosphine–boranes. Consequently, a study of $(CH_3)_3P \cdot BH_3$ and $CH_3PH_2 \cdot BH_3$ was undertaken in order to relate their structures and stabilities to other phosphorus–boron compounds. Since these adducts are stable toward dissociation, it was of particular interest to compare their P–B bond distances to that in $F_3P \cdot BH_3$ which is extensively dissociated at room temperature.

A detailed structural determination of $CH_3PH_2 \cdot BH_3$ was also prompted by the recent study of $HF_2P \cdot BH_3$ which found a pronounced tilt of the borane group away from the fluorine atoms.[4] Since both adducts contain an asymmetrically substituted phosphorus atom, it was hoped that the structural results for $CH_3PH_2 \cdot BH_3$ would aid in identifying the origin of the tilt found in $HF_2P \cdot BH_3$.

Experimental Section

Apparatus.—The spectra were measured with a Stark-modulation microwave spectrometer which employed 80-kHz square-wave modulation.[5] The transition frequencies were measured using both oscilloscope display and pen recordings. The recordings were obtained by using a gear assembly to sweep the klystron slowly through a narrow frequency range. The frequencies were measured directly from the traces which were marked at frequency intervals of 1.0 MHz. All measurements were made at about 0°. The transitions for $(CH_3)_3P \cdot BH_3$ and its isotopic species were reproducible to ±0.2 MHz except for the $(CH_3)_3BH_2D$ species where the uncertainties were ±0.3 MHz. The transitions for the $CH_3PH_2 \cdot BH_3$ species were measured with a precision of about ±0.1 MHz.

Materials.—The $(CH_3)_3P \cdot BH_3$ was prepared by the reaction of $(CH_3)_3P$ with B_2H_6.[1] The spectra of both $(CH_3)_3P \cdot {}^{11}BH_3$ and $(CH_3)_3P \cdot {}^{10}BH_3$ were obtained from this sample. The $(CD_3)(CH_3)_2P \cdot BH_3$ was prepared by allowing $(CD_3)(CH_3)_2P$ to react with B_2H_6. The $(CD_3)(CH_3)_2P$ was prepared by treating $(CH_3)_2PH$ with 99.5% CD_3I.[6] The $(CH_3)_3P \cdot BH_2D$ was prepared by allowing $(CH_3)_3P$ to react with a gaseous mixture consisting of two parts B_2H_6 and one part B_2D_6. This diborane mix-

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