**728.** *A Study of Metal Borohydrides. The Reaction of Aluminium Borohydride with various Ligand Molecules*

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The reactions of aluminium borohydride with several Lewis bases, containing donor atoms from Groups V and VI, have been studied. All the bases react initially to form 1 : 1 adducts, and those containing nitrogen or phosphorus as the donor atom then react further until 4 equivalents of ligand have been consumed; the products are then derivatives of aluminium hydride, $L \to AlH_3$ (where L = ligand) and borane, $L \to BH_3$. The infrared and the proton and ^{11}B nuclear magnetic resonance (n.m.r.) spectra of the products have been recorded, and are discussed in relation to the structure of the adducts. In addition, a comparison of the behaviour of aluminium borohydride with that of the boron hydrides is made.

THE reactions of aluminium borohydride with trimethylamine, dimethyl ether, and ammonia have been reported [1] to form 1 : 1 adducts, but the final products were not fully characterised. The reaction with ammonia has been re-investigated,[2] but without definite conclusions about the nature of the product. More recently, a series of hydro-aluminium borohydride derivatives have been prepared [3] by reaction of the corresponding chloro-derivative with lithium borohydride, and the 1 : 1 adduct with trimethylamine, $Al(BH_4)_3,NMe_3$, was similarly prepared from $AlCl_3,NMe_3$.

We have studied the reaction of aluminium borohydride with the typical Lewis bases, trimethylamine and triethylamine, trimethylphosphine, trimethylarsine, dimethyl ether and diethyl ether, and dimethyl sulphide. In every case, under suitable conditions, the initial attack occurred at the aluminium atom, with the formation of a 1 : 1 adduct.

$$Al(BH_4)_3 \quad \overset{MR_3}{\nearrow} \quad R_3M,Al(BH_4)_3$$
$$\underset{M'R_2}{\searrow} \quad R_2M',Al(BH_4)_3$$
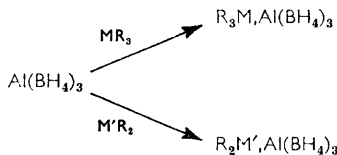
(where M = N, P, or As; M' = O or S; R = alkyl)

For the ligands containing nitrogen or phosphorus atoms, further addition of the base then caused successive cleavage of the Al–H–B bridges yielding finally borane, and aluminium hydride derivatives. Tensiometric titrations showed a sharp break after four equivalents of ligand had reacted. The reaction can be represented by

$$Al(BH_4)_3 + 4MR_3 \longrightarrow 3R_3M,BH_3 + R_3M,AlH_3$$

(where M = N or P; R = alkyl).

The most satisfactory solvent (for the reactions with ligands containing nitrogen, phosphorus, and arsenic) was found to be n-heptane, when the 1 : 1 adducts were precipitated at $-78°$; after removal of solvent the white solid products could be purified by sublimation *in vacuo*. The 1 : 1 adducts with the ligands containing oxygen and sulphur were colourless liquids, and were prepared directly by mixing the two reactants at $-78°$, no further purification being necessary. All the 1 : 1 adducts decomposed very slowly at room temperature, but rapidly at temperatures above about $50°$. They all reacted violently with water (the nitrogen and phosphorus compounds inflaming), and were oxidised in air.

Spectroscopic Studies.—The infrared spectra of all the compounds have been recorded

[1] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Amer. Chem. Soc.*, 1940, **62**, 3421.
[2] L. Taylor, U.S. Dept. Comm., Office Tech. Serv., 1961 A.D., 256, 887, pp. 30—32.
[3] J. K. Ruff, *Inorg. Chem.*, 1963, **2**, 515.

over the range 4000—400 cm.$^{-1}$, although it was difficult to resolve the bands in the 600—400 cm.$^{-1}$ region, since the spectra had to be recorded from mulls or solution. Interpretation of the spectra was simplified by the fact that the bands due to the ligand molecules were always weak in relation to the bands associated with the framework around the aluminium atom. Such behaviour is not unusual in adducts of this type.[4]
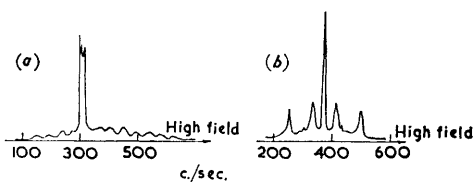
Proton n.m.r. spectrum of
(a) $Al(BH_4)_3,NMe_3$ and (b)
$Al(BH_4)_3,AsMe_3$.

The n.m.r. results (for both the boron-11 nuclei and the protons) are given in the Table, and the Figure shows the proton spectra for the trimethylamine (a) and the trimethylarsine (b) 1 : 1 adducts. These spectra are also similar to that of aluminium borohydride, with the

Magnetic resonance spectra

Compound	Protons						Boron-11	
	Alkyl groups		Borohydride					
	$10^6\delta$	J_{HH}	$10^6\delta$	J_{BH}	J_{AlH}		$10^6\delta$	J_{BH}
$Me_3N,Al(BH_4)_3$ ...	5·18	Not resolved ^{a}	6·50	88	44		54·8 ^{c}	85
$Me_3P,Al(BH_4)_3$ ...	6·3	Not resolved ^{a}	6·60 ^{bg}	—	—		53·6 ^{c}	87·6
$Me_3As,Al(BH_4)_3$ ...	6·26	—	6·32	87	—		53·7 ^{c}	87·8
$Me_2O,Al(BH_4)_3$ ...	4·00	—	6·53 ^{bg}	—	—		—	—
$Et_2O,Al(BH_4)_3$ ...	3·08 ^{d}	7 ^{d}	6·75 ^{bg}	—	—		53·8 ^{c}	85
	6·00 ^{e}	7 ^{e}						
$Me_2S,Al(BH_4)_3$ ...	5·38	—	6·46	87	—		—	—
$Al(BH_4)_3{}^f$	—	—	7·0 ^{h}	87	44		55·1 ^{c}	86

^{a} Unresolved multiplet with signal width of 15 c./sec. $[Me_3N,Al(BH_4)_3]$ and 12 c./sec. $[Me_3P,Al(BH_4)_3]$. ^{b} Broad signal (~500 c./sec.) unresolved. ^{c} Quintuplet. ^{d} Quartet (CH_2). ^{e} Triplet (CH_3). ^{f} See refs. 3 and 5. ^{g} Owing to broad signal, an error of ±0·05 p.p.m. should be allowed. ^{h} Shift with reference to protons in liquid water.

significant difference that, firstly, for the trimethylamine adduct, the proton resonance for the borohydride groups has been partially resolved into twelve resonances of relative intensities 1 : 1 : 2 : 2 : 3 : 3 : 3 : 3 : 2 : 2 : 1 : 1; resolution of the proton signal has only been observed previously for aluminium borohydride itself [5] by saturating the aluminium-27 resonance, when the resultant quartet was identical with that obtained for the borohydride ion, although saturation of the boron-11 resonance did not produce the sextet expected, but only a partially resolved multiplet. Secondly, the proton spectra of the trimethylarsine and dimethyl sulphide adducts also show some resolution into four prominent lines similar to that obtained for the borohydride ion.

RESULTS AND DISCUSSION

The nuclear magnetic resonance and infrared studies, as discussed below, together with the stoicheiometry of the reactions, indicate that the ligand co-ordinates first with the aluminium atom, thus substantiating earlier suggestions of an aluminium-ligand atom bond in the 1 : 1 adducts.[3]

The physical properties of aluminium borohydride (b. p. 44·5°, m. p. —64·5°) suggest that it is predominantly covalent in character. Studies on the structure and bonding in metal borohydrides indicate that the more covalent, such as aluminium and beryllium,

[4] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Proc. Chem. Soc.*, 1962, 249.
[5] R. A. Ogg and J. D. Ray, *Discuss. Faraday Soc.*, 1955, **19**, 239.

are similar in many respects to the boron hydrides. Thus electron diffraction,[6] infrared,[7] Raman,[8] and n.m.r. spectra [5] support the conclusion that, for aluminium borohydride, the central aluminium atom is surrounded by three borohydride groups with a planar AlB_3 skeleton, and with two hydrogen atoms of each borohydride group being bridged between the aluminium and boron atoms.

On formation of the 1 : 1 adducts, the arrangement around the aluminium presumably changes from planar, AlB_3, to tetrahedral, $L{\rightarrow}AlB_3$, with the ligand atom occupying the fourth tetrahedral position. The trimethylamine and trimethylphosphine compounds are essentially monomeric in 0·1M-benzene solution, the degrees of association, measured cryoscopically, being 1·13 and 1·19, respectively. Such association probably arises from the dipole–dipole interaction expected in such structures. Although the aluminium would appear to be seven-co-ordinate in such a structure, it is possible to construct the double hydride bridge structure with only one bonding orbital on the aluminium atom per borohydride group.[3] The exact positions of the bridge hydrogen atoms cannot be determined from the experimental evidence so far reported, and a more detailed spectroscopic examination of the adducts is desirable, although such studies alone would probably not differentiate between the tetrahedral structures with C_{3v} and C_3 symmetry; in the latter case, the bridge hydrogens would be twisted out of the L–Al–B plane.

All the adducts show striking similarities in their infrared spectra: thus, all resembled the spectrum of aluminium borohydride over the region 4000—1100 cm.$^{-1}$, while over the region 1100—400 cm.$^{-1}$ each compound showed at least three major bands. With the adducts with nitrogen or oxygen as the donor atom, a further band was observed at about 500 cm.$^{-1}$, which presumably arises from the Al–O or Al–N stretching mode, since Al–N stretching frequencies have been reported in this region.[9] Unfortunately, this frequency always overlapped with the rather broad band at about 500—400 cm.$^{-1}$, and could not therefore be resolved. The only other adduct that showed more than three bands in this region was that with diethyl ether, where one extra band was observed. Whether the bands in the 1100—400 cm.$^{-1}$ region are associated with the bridge hydrogens or only with the L$\rightarrow$AlB$_3$ framework cannot be determined at present. The presence of L$\rightarrow$AlH$_3$ and L$\rightarrow$BH$_3$ derivatives in the products after four equivalents of base had reacted was confirmed by comparison with published spectra (L$\rightarrow$AlH$_3$),[9] and spectra of prepared pure samples (L$\rightarrow$BH$_3$).

The equivalence of the four hydrogen atoms around the boron atom is shown by the quintet observed in the boron-11 nuclear magnetic resonance spectra of the 1 : 1 adducts with trimethylamine, trimethylphosphine, trimethylarsine, and diethyl ether. This, together with the infrared spectra, supports the structure involving an aluminium–ligand atom bond, and suggests that the bonding of the borohydride group is similar in both the aluminium borohydride and the complexes. The proton spectra exhibit some interesting features in that, while the signals were usually broad and unresolved, the signal from the complexes involving trimethylamine, trimethylarsine, and dimethyl sulphide show considerable splitting, and it is therefore possible to obtain reliable values for the shift and coupling constants of the protons. The splittings for the trimethylamine adducts were significantly different from those for the trimethylarsine and dimethyl sulphide adducts. In the former, the signal was split into twelve lines, and it appears that these represent the twenty–four lines expected, from spin–spin interaction with the aluminium-27 and boron-11 nuclei, which have spin-quantum numbers of $\frac{5}{2}$ and $\frac{3}{2}$, respectively, allowing for coincidences. In the latter case, the borohydride protons were split into four prominent lines and, if these represent spin–spin coupling with the boron-11 nuclei, the splitting due to coupling with the

[6] J. Y. Beach and S. H. Bauer, *J. Amer. Chem. Soc.*, 1940, **62**, 3440; S. H. Bauer, *ibid.*, 1950, **72**, 622.
[7] W. C. Price, *J. Chem. Phys.*, 1949, **17**, 1044.
[8] A. R. Emery and R. C. Taylor, *Spectrochim. Acta*, 1960, **16**, 1455.
[9] G. W. Frazer, N. N. Greenwood, and B. P. Straughan, *J.*, 1963, 3742.

aluminium nuclei is apparently unresolved or absent, since integration over the borohydride and methyl protons confirms that the ratio is 12 : 9 for $Al(BH_4)_3,AsMe_3$ and 12 : 6 for $Al(BH_4)_3,SMe_2$, respectively. In the spectra of the remaining adducts, the line-broadening for the borohydride protons is presumably due to quadrupole coupling with the aluminium and boron nuclei.

The boron-11 spectra also confirm that the 1 : 1 adducts contain no cleavage products (*i.e.*, L→BH₃ derivatives), and that after four equivalents of the nitrogen and phosphorus bases have reacted with aluminium borohydride, no borohydride groups remain, since a 1 : 3 : 3 : 1 quartet is then obtained. The protons in the aluminium hydride derivatives (L→AlH₃) were not detected over a sweep of 500 c./sec. to high field and 1000 c./sec. to low field of the borane proton signal.

In view of the relatively small changes in the proton line on adduct formation, it is not surprising that changes in the boron-11 spectra are also small. Indeed, there is a remarkable consistency in both the chemical shifts and coupling constants for the boron atom in the adducts, compared with that in aluminium borohydride, not only in the compounds reported here, but also in a variety of hydrido-aluminium borohydride adducts reported previously.[3] Definite conclusions cannot be made until more values on similar systems are available, but comparison with the boron hydrides reveals that here also boron atoms adjacent to the centre of substitution may be equally uninfluenced: thus, in pentaborane-9, halogen substitution on the apex boron hardly affects the shift and coupling constants of the base boron atoms.[10]

A comparison of the behaviour of aluminium borohydride with that of diborane is interesting. The bases trimethylamine,[11] triethylamine,[12] trimethylphosphine,[13] and trimethylarsine [14] all cleave diborane (yielding L→BH₃ derivatives) even at −78°, while dimethyl ether,[15] diethyl ether,[16] and dimethyl sulphide [17] form complexes, that are unstable at 25° and dissociate reversibly. However, with the borohydride, only trimethylamine reacted rapidly at 25° to cleave every bridge, while triethylamine reacted over a period of hours, and trimethylphosphine over a period of several days in the same way. Trimethylarsine reacted rapidly at 25° to form the 1 : 1 adduct, but then did not react further, and the ligands containing oxygen and sulphur atoms reacted similarly. These differences probably arise from the different charge distribution in the Al−H−B bridges compared with that in diborane. Although the bonding of the bridge atoms appears similar in each case, it is to be expected, that, since aluminium has a lower electronegativity than boron (B, 2·0; Al, 1·5), the charge-distribution would no longer be symmetrical, as in diborane, but would now favour the boron atom, thus making the aluminium atom more susceptible to nucleophilic attack.

EXPERIMENTAL

Preparations and operations were carried out in a conventional vacuum-line, or in a glove box filled with dry, oxygen-free, nitrogen. Solvents were dried over a molecular sieve (type 4A), and then distilled from lithium aluminium hydride. Trimethylphosphine [18] and trimethylarsine [19] were prepared from methylmagnesium iodide as described previously. The remaining ligands were dried over lithium aluminium hydride, and distilled *in vacuo*. Trimethylamine and triethylamine were first purified by treatment with toluene-*p*-sulphonyl chloride.

Preparation of Aluminium Borohydride.—The method of Brown and his co-workers was

[10] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, 1959, **63**, 1533.
[11] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780.
[12] H. C. Brown, U.S.P. 2,860,167/1958.
[13] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.
[14] F. G. A. Stone and A. B. Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 386.
[15] H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 290.
[16] F. G. A. Stone, *Chem. Rev.*, 1958, **58**, 101.
[17] W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164.
[18] L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, 1957, **53**, 1606.
[19] L. H. Long and J. F. Sackman, *Trans. Faraday Soc.*, 1956, **52**, 1201.

used.[20] The product was purified by distillation *in vacuo* (v.p. of purified product at $0^\circ =$ 119·5 mm. was identical with that previously reported [1]), and yields of 60—70% theoretical were obtained.

Preparation of the 1 : 1 *Adducts.*—Two methods were employed, one for the ligands containing nitrogen, phosphorus, and arsenic, the other for the oxygen and sulphur compounds. For the former, a typical procedure was as follows: aluminium borohydride (1·2 g., 16·8 mmole) was condensed on to about 100 ml. of n-heptane at -78°, and trimethylamine (0·8 g., 13·6 mmole) slowly added with stirring. The solvent and excess of borohydride were removed from the precipitate *in vacuo* at room temperature, and the residue purified by sublimation *in vacuo* at 35° yielding crystals, m. p. (sealed tube) 78—80° (lit.,[1] 79°). Apparent decomposition on heating prevented a more accurate determination (Found: Al, 19·9; active H, 9·05; B, 25·3; Me$_3$N, 44·5. $C_3H_{21}AlB_3N$ requires Al, 20·7; active H, 9·2; B, 24·8; Me$_3$N, 45·2%). The hitherto unreported trimethylphosphine and trimethylarsine derivatives were similarly purified and obtained as crystals with m. p. 78 and 57°, respectively (Found: Al, 18·1; active H, 8·2; B, 23·2. $C_3H_{21}AlB_3P$ requires Al, 18·1; active H, 8·1; B, 22·1%. Found: Al, 14·1; active H, 6·35. $C_3H_{21}AlB_3As$ requires Al, 14·1, active H, 6·3%).

A typical preparation for the sulphide and ether adducts was as follows: diethyl ether (0·92 g., 12·4 mmole) was condensed on to aluminium borohydride (0·89 g., 12·4 mmole) at 196°, and the mixture allowed to warm slowly to room temperature. An involatile liquid (m. p. -15 to -14°) remained and no volatile material could be recovered from the reaction flask. The adducts with dimethyl ether (m. p. 0 to $+1^\circ$) and dimethyl sulphide (m. p. $-0·5$ to $+1·5^\circ$) were similar.

Molecular Weight Determinations.—The molecular weights were determined cryoscopically in benzene solution by the method previously described.[21] The apparatus was modified so that the solutions prepared in the dry box could be introduced with a syringe.

Analytical Methods.—Active hydrogen was determined gas-volumetrically after hydrolysis of the adduct with 2M-hydrochloric acid in a sealed-off bulb fitted with a break-seal. The bulb was heated at 50° for 12 hr. to ensure complete hydrolysis. After removal of the hydrogen, the contents of the bulb were dissolved in a known volume of water, and the aluminium determined by means of 8-hydroxyquinoline, and the boron by distillation as methyl borate. The trimethylamine was determined by rendering a portion of the solution alkaline with sodium hydroxide, distilling the base into standard hydrochloric acid, and back-titrating.

Infrared Spectra.—Measurements were made over the region 4000—375 cm.$^{-1}$ with an S.P. 100 spectrophotometer, and with Perkin-Elmer model 137 Infracords with sodium chloride and potassium bromide optics. The solid samples were measured in Nujol and hexachloro-butadiene mulls, and in benzene solution, and the liquid samples as thin liquid films. The following values for the compounds include, where applicable, the Nujol bands, and bands that were obtained by other means are marked appropriately, *i.e.*, bands obtained with hexachloro-butadiene mulls marked (*), and those obtained with benzene solutions marked (†).

Me$_3$N,Al(BH$_4$)$_3$: 3020w, 2995s, 2952—2853vs br, (2995vwsh*, 2910w*, 2860wsh*), 2515s, 2439s, 2150s, 1465vs, 1420ssh, 1385s, (1460s,* 1420m*), 1289m, 1239m, 1179w, 1120s, 1110s, 980s, 859w, 815s, 728w, 540s, 495sbr cm.$^{-1}$.

Me$_3$P,Al(BH$_4$)$_3$: 2951ssh, 2915s, 2855s, (2912w†), 2490s, 2420s, 2225s, 2107s, 1465vs, 1421s, 1385vs, (1433sbr†), 1317m, 1299m, 1172w, 1115s, 988m, 955s, 855w, 755m, 725w, 495s, 440msh cm.$^{-1}$.

Me$_3$As,Al(BH$_4$)$_3$: 2960s, 2930s, 2865s, 2476s, 2425s, 2132s, 1465s, 1420s, 1385s, (1420s*), 1275m, 1146m, 1119s, 980w, 916s, 837w, 628m, 482s, 417s cm.$^{-1}$.

Me$_2$O,Al(BH$_4$)$_3$ (liq. film): 2905vw, 2495s, 2430s, 2130s, 1445s, 1255w, 1150wsh, 1115s, 1005s, 867s, 520s, 470sbr cm.$^{-1}$.

Et$_2$O,Al(BH$_4$)$_3$ (liq. film): 3010w, 2990w, 2943vw, 2914vw, 2878vw, 2500s, 2435s, 2225msh, 2150s, 1640vvw, 1470s, 1448s, 1398m, 1330w, 1289w, 1192w, 1150w, 1119s, 1092w, 1005s, 882s, 830w, 800w, 769s, 520mbr, 490mbr cm.$^{-1}$.

Me$_2$S,Al(BH$_4$)$_3$ (liq. film): 2895vw, 2800vw, 2460vs, 2410vs, 2270msh, 2205msh, 2150ssh, 2115vs, 1460msh, 1415vs, 1265w, 1139vs, 1105m, 1095msh, 1035s, 990m, 675vw, 480s, 415mbr cm.$^{-1}$.

High-resolution Nuclear Magnetic Resonance Spectra.—Measurements were made on a Varian

[20] H. C. Brown, H. I. Schlesinger, and E. K. Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 209.
[21] H. P. Treffers and L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1708.

Associates model A60 (at 60 Mc./sec. and $20° \pm 2°$ for protons) and Associated Electrical Industries R.S.2 (at 20 Mc./sec. and $22° \pm 2°$ for boron-11) spectrometers. The compounds were dissolved in benzene, except for the measurement of the boron-11 spectra of the liquid adducts, where pure liquids were used. For the proton spectra, the chemical shifts were measured relative to benzene, and trimethyl borate used as an external reference in the boron-11 spectra. Line positions were determined by conventional side-band techniqes.

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