# Spectroscopic Studies on Derivatives of Aluminium Borohydride
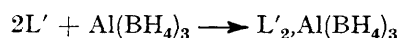
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The assignment of group frequencies in the i.r. spectra of derivatives of aluminium borohydride has been made by the use of aluminium borodeuteride. Variations in the spectra with the change of ligand are discussed. The properties of the compounds in solutions have been studied using ${}^1H$ n.m.r. spectroscopy, and data obtained over a range of temperature indicate that the 1:1 adducts with trimethylamine and trimethylphosphine dissociate in solution, and probably exist in equilibrium with both the 1:2 adducts, e.g. $Al(BH_4)_3.2NMe_3$ and free aluminium borohydride.
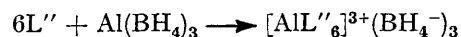
ALUMINIUM borohydride, $Al(BH_4)_3$, combines with ligand molecules to form co-ordination compounds (only those stable at ambient temperatures are considered in this paper) which vary in stoicheiometry and type [1,2] e.g.,

$$L + Al(BH_4)_3 \longrightarrow L,Al(BH_4)_3$$
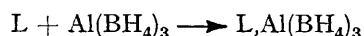
(where L = NMe_3, PMe_3, PPh_3, $AsMe_3$, Me_2O, Et_2O, or Me_2S)

$$2L' + Al(BH_4)_3 \longrightarrow L'_2,Al(BH_4)_3$$

(where $L' = PMe_3$, NH_3)

$$6L'' + Al(BH_4)_3 \longrightarrow [AlL''_6]^{3+}(BH_4^-)_3$$

(where $L'' = NH_3$)

Since the i.r. spectra of these compounds provide useful information on the bonding of the borohydride

[1] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc.*, 1965, 3923.
[2] P. H. Bird and M. G. H. Wallbridge, *J. Chem. Soc. (A)*, 1967, 664.

group further data have been obtained on the adducts with triphenylphosphine, ammonia (both 1 : 2 and 1 : 6 adducts), and trimethylphosphine (1 : 2 adduct). In addition, the spectra of the above adducts with aluminium borodeuteride, $Al(BD_4)_3$, except those with diethyl ether, triphenylphosphine, and the 1 : 6 adduct with ammonia, have been recorded. For the last mentioned the product obtained with deuteriated ammonia *i.e.*, $Al(BH_4)_3,6ND_3$, has been studied. Previous studies [1] of the ^{1}H and [11]B n.m.r. spectra of the 1 : 1 adducts have shown that a rapid exchange of the bridging and terminal protons of the borohydride group occurs rendering all the protons equivalent. The protons are then coupled to both the boron (for [11]B, $I = 3/2$) and aluminium (for [27]Al, $I = 5/2$) nuclei, and a 24-line multiplet is obsrved in the [1]H n.m.r. spectrum. Such spectra therefore usefully augment the i.r. spectra in that they provide a further indication as to whether the borohydride group is bonded through bridging hydrogen atoms, or exists as a discrete ion, BH_4^-. The ^{1}H spectra of the trimethylamine and trimethylphosphine 1 : 1 adducts have been further studied over a temperature range for the reasons outline in the discussion below.

RESULTS AND DISCUSSION

All the 1 : 1 and 1 : 2 adducts show i.r. spectra which are very similar in their general features when considering the frequencies associated with the aluminium borohydride portion of the molecule, and typical spectra are shown in Figure 1. These results, together with the equivalence of the three boron nuclei in all the [11]B n.m.r. spectra, suggest that the 1 : 1 adducts have similar structures with the ligand atom bonded to the aluminium atom [1] (Figure 2). The presence of such a bond has been confirmed for the trimethylamine [3,4] and trimethylarsine [5] adducts by *X*-ray crystallographic structure determinations. On the basis of the i.r. data so far obtained it is not feasible to deduce the structure unambiguously since (*a*) most of the skeletal modes occur below 375 cm.[-1] (the limit of the spectra reported here), and (*b*) it has not yet been possible to resolve all the bands associated with borohydride groups. Even if far-i.r. and Raman data were obtained it would still be very difficult to distinguish between the different possible symmetries of the adducts, a similar problem having been encountered with the spectra of aluminium borohydride itself.[6]

However, the deuteration studies do permit a classification of the observed frequencies into three main types: (I) Bands arising from vibrations within the aluminium borohydride fragment of the adduct. The general assignments are given in Table 1.

(II) Absorptions due to the stretching mode associated with the aluminium–ligand atom bond were not observed in the 4000—400 cm.[-1] region, except for possibly the

Al–N, Al–O frequencies. It is probable that these vibrations are not pure stretching modes, but for example are mixed with other vibrations associated with
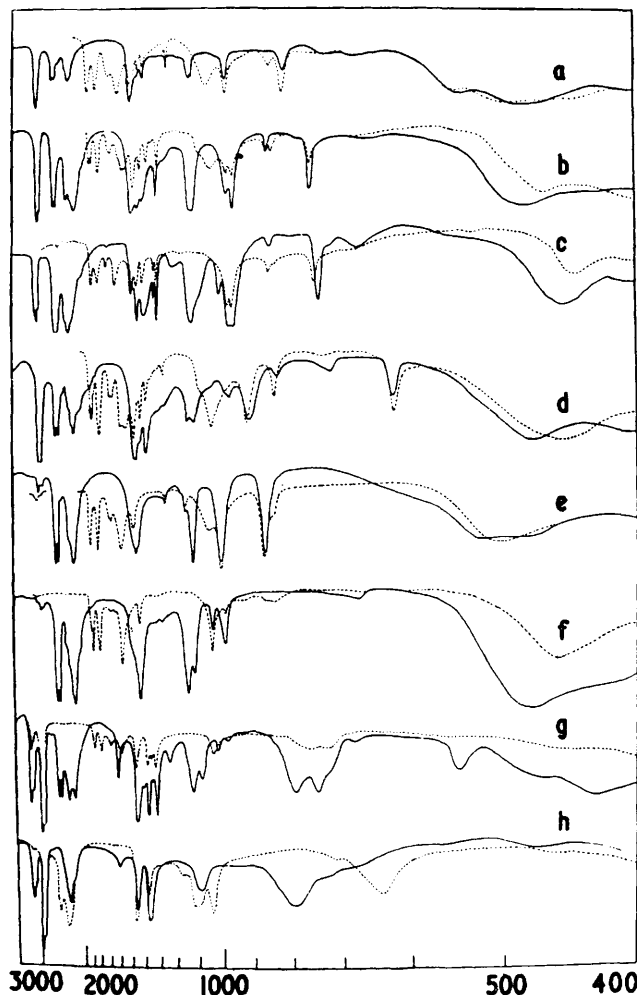

FIGURE 1   The i.r. spectra of aluminium borohydride (——) and borodeuteride (– – – –) derivatives

(a) $Al(BH_4)_3,NMe_3$; (b) $Al(BH_4)_3,PMe_3$; (c) $Al(BH_4)_3,2PMe_3$; (d) $Al(BH_4)_3,AsMe_3$; (e) $Al(BH_4)_3,OMe_2$; (f) $Al(BH_4)_3,SMe_2$; (g) $Al(BH_4)_3,2NH_3$; (h) $Al(NH_3)_6,(BH_4)_3$ and $Al(ND_3)_6,(BH_4)_3$. The spectra are recorded from Nujol mulls except for (e) and (f) where the pure liquid was used as a liquid film
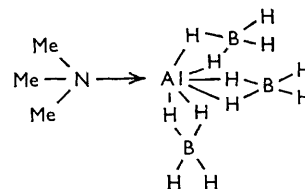

FIGURE 2

the AlH_2B bridge system. They are also difficult to identify unambiguously since they appear to overlap

[3] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Comm.*, 1965, 438.
[4] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Comm.*, 1966, 286.

[5] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Inorg. Chem.*, 1968, in the press.
[6] A. R. Emery and R. C. Taylor, *Spectrochim. Acta*, 1960, 16, 1455.

with the AlB_3 vibration (discussed below), but they may tentatively be assigned to bands in the 500—400 cm.$^{-1}$ portion of the spectrum. The remaining aluminium–ligand atom vibrations are assumed to lie below 400 cm.$^{-1}$.

(III) The remaining bands are then associated with the vibrations within the ligands. These do not shift

TABLE 1

Assignments of group frequencies associated with aluminium borohydride in various adducts (cm.$^{-1}$)

Adducts with	Terminal B–H	BH$_2$ Def.	Bridge str. (asym.) and expansion	Bridge str. (sym.)	$Al{\displaystyle{<}}^{B}_{B}$ str. (asym.)
Al(BH$_4$)$_3$	2520—2360	1140—1105	2260—2090	1490—1370	490—450
Al(BD$_4$)$_3$	1900—1760	870—840	1670—1510	1060—1030	460—440

* In the free borohydride these bands appear at 602 cm.$^{-1}$ for Al(BH$_4$)$_3$ and 569 cm.$^{-1}$ for Al(BD$_4$)$_3$.

appreciably on deuteriation of the borohydride, and may, in general, be identified by comparison with the absorptions of the free ligand molecule.

It has been suggested [7] that the two vibrations associated with the B–H terminal and bridging modes in diborane (at 2614 and ca. 1900 cm.$^{-1}$ respectively) may be regarded as having become degenerate in the BH_4^- ion at 2270 cm.$^{-1}$, and that aluminium borohydride lies between these two extremes showing two frequencies at 2559 and 2031 cm.$^{-1}$. The tendency of the borohydride group to acquire more ionic character in aluminium borohydride compared with that in diborane to further reflected in the configurations of the BH_4 group in the two molecules.[8,9]
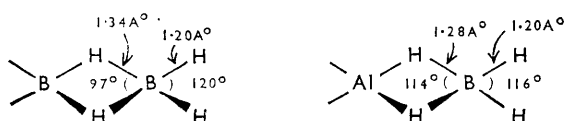

FIGURE 3   Geometries of the BH_4 group in diborane and aluminium borohydride

It is therefore of interest to examine the frequencies arising from the borohydride protons in the 1 : 1 adducts reported here since the donation of electron density which is being made to the aluminium atom would be expected to be delocalised into the borohydride group resulting in a concomitant change in the hybridisation of the boron atoms towards that in the borohydride ion. Thus, the stretching modes of both the terminal B–H bonds would be expected to decrease and the bridging AlH_2B bonds to increase towards 2270 cm.$^{-1}$. The experimental values, given in Tables 2 and 3, confirm

[7] W. C. Price, J. Chem. Phys., 1949, **17**, 1044.
[8] L. S. Bartell and B. L. Carroll, J. Chem. Phys., 1965, **42**, 1135.

that such a trend exists, and also show that a proportionately longer shift is observed for both frequencies, as expected, on going from the 1 : 1 to 1 : 2 adduct trimethylphosphine.

The ^1H and ^{11}B n.m.r. spectra for both the borohydride and ligand protons have been reported.[1] In general, the signals from the ligand protons are sharp singlets for the methyl groups, and the triplet and quartet expected for the ethyl groups. We have observed, however, that the signals from trimethylamine and trimethylphosphine in the 1 : 1 adducts are broad (ca. 15 c./sec.) at room temperature, and two intensity

TABLE 2

Variations of the B–H (terminal) stretching frequencies in various borohydride derivatives

Compound	B–H (asym.) (cm.$^{-1}$)	B–H (sym) (cm.$^{-1}$)
Al(BH$_4$)$_3$	2559	2493
Al(BH$_4$)$_3$,NMe$_3$	2515	2439
Al(BH$_4$)$_3$,PPh$_3$	2505	2440
Al(BH$_4$)$_3$,PMe$_3$	2490	2420
Al(BH$_4$)$_3$,AsMe$_3$	2476	2425
Al(BH$_4$)$_3$,Et$_2$O	2500	2435
Al(BH$_4$)$_3$,Me$_2$O	2495	2430
Al(BH$_4$)$_3$,Me$_2$S	2460	2410
Al(BH$_4$)$_3$,2PMe$_3$	2448	2363
B$_2$H$_6$	2614	2522
LiBH$_4$	2320	
NaBH$_4$	2270	

TABLE 3

Bridge stretching frequencies for 1 : 1 adducts of aluminium borohydride

Ligand (cm.$^{-1}$)	Al(BH$_4$)$_3$	NMe$_3$	PMe$_3$	PPh$_3$	AsMe$_3$	2PMe$_3$
	2031	2150	2107	2132	2132	2165
Ligand (cm.$^{-1}$)	Me$_2$O	Et$_2$O	Me$_2$S	2NH$_3$		
	2130	2150	2150	2200—2140		

maxima for the former adduct suggested the signal might be a doublet. In view of this unusual behaviour, we have extended our previous studies by studying the
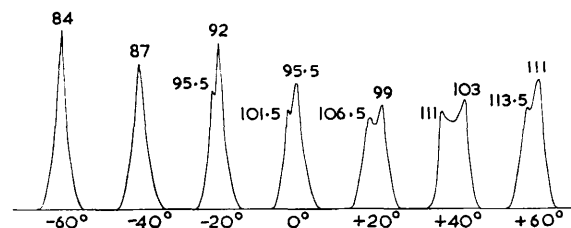

FIGURE 4   The variation in signal shape for the methyl protons in the proton n.m.r. spectrum of aluminium borohydride–trimethylamine over the temperature range −60 to +60°. The numbers adjoining the peaks represent the shift in c./secs downfield from TMS

variation in the signals from these two adducts over the temperature range −60° to +60°. The variation in signal shape for the trimethylamine adduct is shown in Figure 4. Such spectra suggest the presence of at least

[9] A. Almenningen, G. Gundersen, and A. Haaland, Acta Chem. Scand., 1968, **22**, 328.

two different environments for the ligand protons, each environment showing a characteristic chemical shift. The rather broad signals suggest the possibility of an exchange process occurring at the higher temperatures, probably involving both the 1 : 1 and 2 : 1 adducts as

$$2Al(BH_4)_3,L \rightleftharpoons Al(BH_4)_3,2L + Al(BH_4)_3$$
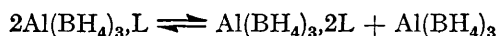
giving rise to the change in signal shape typical of such an exchange process.[10] The signal at $-60°$ may therefore be assumed to arise from the undissociated 1 : 1 adduct, and the two signals obtained at $+60°$ from the 1 : 1 and 2 : 1 adducts. The new signal which appears at the higher temperatures cannot satisfactorily be assigned to other sources such as free trimethylamine or trimethylamine–borane (arising from a cleavage reaction) since the signal from the former appears at -2.08 p.p.m., and that from the latter at -2.21 p.p.m. in benzene solution. Thus other possible schemes such as

$$Al(BH_4)_3,L \rightleftharpoons Al(BH_4)_3 + L$$

or

$$Al(BH_4)_3,L \longrightarrow Al(H)(BH_4)_2 + H_3B,L$$
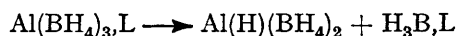
appear unlikely. The trimethylphosphine adduct shows similar behaviour, the broad unresolved signal at $25°$ being resolved into a sharp doublet (due to coupling with the ^{31}P nucleus, J_{P-H} 5 c./sec.) below $-35°$, and a broader doublet above $+60°$.

An alternative explanation of the results is possible if it is assumed that the signal obtained at $25°$ consists of two signals arising from two different intramolecular environments of the ligand protons. For example, either an arrangement whereby the ligand molecule has a different orientation with respect to the AlB_3 framework (e.g., staggered or eclipsed) in two separate molecules, or a hindered rotation of the methyl protons could be postulated. The effect on the signal shape when the temperature was lowered would then be due to differences in the relative chemical shift of the signal from each species such that the chemical shift of the signals observed at $+20°$ become coincident at $-60°$. However, the observed broadening of the signals suggest that the former explanation is the more likely. The variations in the signals for the borohydride groups in the two adducts over the temperature range are less apparent

because the signals are broad (ca. 300 c./sec.), and less well resolved. Thus, both the dodectet of the trimethylamine adduct and the partially resolved multiplet for the trimethylphosphine adduct observed at $25°$ became less well resolved at -60 and $-45°$ respectively, although there was little change in the original spectra on heating the samples to $+80$ and $+60°$ respectively. These results suggest that the exchange between the bridge and terminal borohydride protons may be slower at low temperatures, and it is not unreasonable to assume that at sufficiently low temperatures the signals would become resolved again to show distinct bridge and terminal protons as observed in the spectrum of diborane at room temperature. In each sample the signals from any free aluminium borohydride or 1 : 2 adduct produced would also be broad, with τ values similar to those of the 1 : 1 adducts, and would not therefore be observed as distinct signals.

EXPERIMENTAL

The compounds were prepared as previously described,[1] and were handled in a dry nitrogen-filled glove box in view of their susceptibility to hydrolysis and oxidation. The i.r. spectra were recorded using an SP 100 Unicam spectrophotometer from mulls, or liquid films in the case of the liquid adducts. No significant changes in the spectra were observed when the compounds were run in benzene solution instead of as a Nujol mull.

The n.m.r. spectra over the temperature range were recorded using a Varian A60 spectrometer and perdeuteriotoluene as the solvent. This was the only solvent in which the adducts were sufficiently soluble at low temperatures. The concentrations were ca. 10% w/w, this avoided any significant intermolecular effects arising from dipole–dipole interactions since the chemical shifts were invariant over a concentration range 5—20% w/w.

The aluminium borodeuteride was prepared from lithium borodeuteride using a procedure identical with that used for the borohydride. The adducts were also prepared using the methods described for the borohydride adducts.[1]

[10] J. A. Pople, W. G. Schneider, and H. J. Bernstein, ' High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, London, 1959, p. 223.