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Study of the Interaction of $AlCl_3$ with the $B_{10}H_{10}^{2-}$ Cage in the Solid State

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Abstract

$AlCl_3$ reacts with the hydroborates $M_2B_{10}H_{10}$ (M = Et_4N, Bu_4N, K or Na) in the solid state, the reaction going to completion more rapidly with the tetraalkylammonium salts. The products obtained are dissociated by THF by complexation and dissolution of the $AlCl_3$. The reaction perturbs the BH stretching vibrations and produces an increase of more than 100 cm^{-1} in these frequencies. According to the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio, the IR spectra in the 300–600 cm^{-1} region and the ^{27}Al NMR spectra of the solid resemble those of $AlCl_4^-$ or $Al_2Cl_7^-$. However the results are best interpreted by assuming the formation of $[B_{10}H_{10}(AlCl_3)_2]^{2-}$ with localization of a negative charge in the vicinity of each $AlCl_3$. Subsequent addition of $AlCl_3$ should produce $[B_{10}H_{10}(Al_2Cl_6)_2]^{2-}$.

The same reaction performed in liquid SO_2 after evaporation of the solvent yields solid products which are hazardous to handle.

Introduction

In previous work [1] we have shown that the opening of the $B_{10}H_{10}^{2-}$ cage (see Fig. 3) occurs by hydrolysis of $AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ mixtures and that the decaborane derivative 6-$B_{10}H_{13}Cl$ is obtained selectively in this reaction. A study of the $AlCl_3$–$M_2B_{10}H_{10}$ system has been undertaken with the aim of yielding new information about the previous reaction. It turned out that in the solid state and under anhydrous conditions, $AlCl_3$ interacts with decahydrodecaborates containing the EtN_4^+, Bu_4N^+, K^+ and Na^+ cations. To our knowledge, such an interaction involving closoboranes has neither been described nor predicted in the literature although $AlCl_3$ has been used in many reactions involving boranes and carboranes [2].

The reaction of $AlCl_3$ with decahydrodecaborates yields uncrystallizable solid products. Due to their physical state, their reactivity and the lack of solvents able to dissolve them without decomposition, the methods available for their study were limited.

Results

After having stirred a solid mixture of $AlCl_3$ and a decahydrodecaborate for 10 h at a temperature of less than 70 °C and under perfectly anhydrous conditions, IR spectroscopy showed that the starting materials had been converted into new products. The interactions showed a noticeable increase in the frequencies of the BH stretching vibrations (Fig. 1), but they were not strong enough to prevent a base such as THF reacting with $AlCl_3$ bonded to the hydroborate and dissociating the product formed. Treatment with THF selectively dissolves $AlCl_3$ and the decahydrodecaborate can be recovered. The reaction reaches completion after 10 h at room temperature with Et_4N^+ or Bu_4N^+ but is incomplete at 68 °C with K^+ or Na^+ after a reaction time of 12 h. The tetraethylammonium salt has been used as the standard product in this study, and the particularities observed for the other salts have been mentioned.

Two regions of the IR spectra have proved to be very sensitive to the chemical changes in the solid:

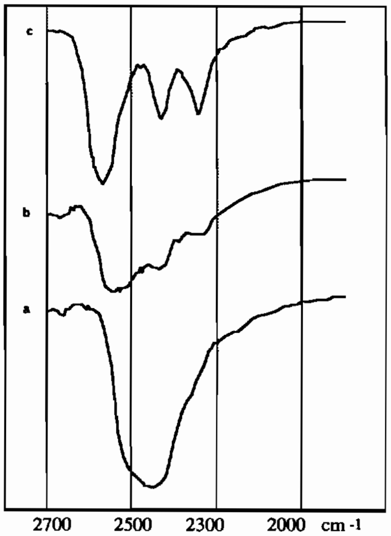

Fig. 1. IR spectra, BH stretching vibration region: a, $(Et_4N)_2B_{10}H_{10}$; b, $AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ in a 2:1 ratio; c, $AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ in a 4:1 ratio.

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the 2200–2700 cm^{-1} region (Fig. 1) which contains the absorption bands due to the BH stretching vibrations, and the 300–600 cm^{-1} region which concerns the AlCl stretching vibrations. The corresponding Raman spectra could not be obtained because of a strong fluorescence of the samples.

With a 1:1 ratio of decahydrodecaborate to $AlCl_3$, the BH absorption is split into two bands of nearly equal intensity, one centred at 2440 cm^{-1} as for $(Et_4N)_2B_{10}H_{10}$ in Fig. 1a and the other at 2505 cm^{-1}. An increase in the BH frequencies is observed with a new addition of $AlCl_3$ to the reaction mixture. The effect produced for a 2:1 ratio is shown in Fig. 1b where the main absorption is at 2545 cm^{-1}. The two shoulders at 2340 and 2435 cm^{-1} are attributed to products containing more than $2AlCl_3$ per $B_{10}H_{10}^{2-}$ and their presence is probably due to the fact that, for thermodynamic or kinetic reasons, the $AlCl_3$ distribution is not perfectly homogenous. The frequency of the main BH absorption increases again when the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio is increased from 2:1 to 4:1 and the two shoulders at 2340 and 2435 cm^{-1} become medium intensity bands. Further addition of $AlCl_3$ has no effect on the position and intensity of these bands.

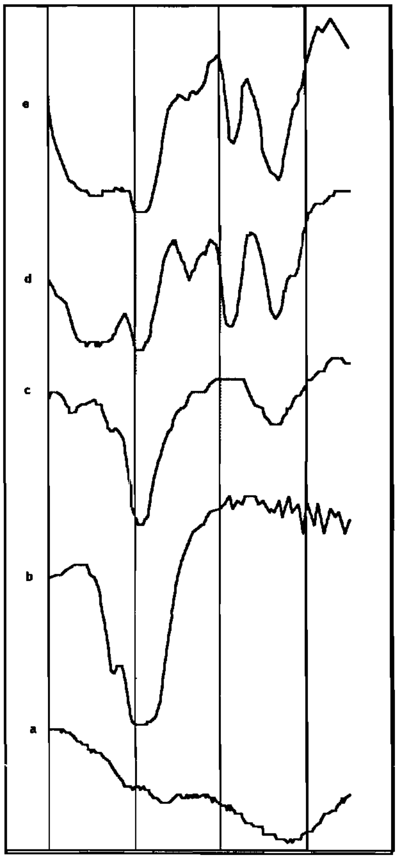

Fig. 2. IR spectra, AlCl stretching vibration region: a, $AlCl_3$; b, $AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ in a 2:1 ratio; c, Et_4NAlCl_4; d, $AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ in a 4:1 ratio; e, $Et_4NAl_2Cl_7$.

TABLE 1. ^{27}Al NMR Data for $(Et_4N)_2B_{10}H_{10}$–$AlCl_3$ Reaction Products, Et_4NAlCl_4, $Et_4NAl_2Cl_7$ and $Et_4NAl_2Cl_7$ Containing an Excess of $AlCl_3$[a]

$AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio	$AlCl_3$ to Cl^- ratio	Position of the 1st peak (ppm)	Position of the 2nd peak (ppm)
1		99.15	
2		99.14	
3		99.12	
4		99.13	
5		99.20	-4.91
6		98.94	-5.14
	1	99.00	
	2	99.10	
	3	98.32	-4.96

[a] $Al(H_2O)_6^{3+}$ was used as reference and the shifts are counted positively in the low field direction.

Because no change occurs in the AlCl frequency region until the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio reaches 2:1 (Fig. 2b), the reaction of $AlCl_3$ with $B_{10}H_{10}^{2-}$ remains the same for these compositions. These spectra are very different from those of molecular complexes of $AlCl_3$ which contain a very strong absorption between 525 and 540 cm^{-1} and a strong absorption between 310 and 330 cm^{-1} [7–9], but the very strong absorption at 492 cm^{-1} resembles that of $AlCl_4^-$ (Fig. 2c). The increase of the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio from 2:1 to 4:1 corresponds to the complete conversion of the previous aluminium species to a new species (Fig. 2d) whose spectrum shows many features common to those of $Al_2Cl_7^-$. Due to the broadness of its main band near 320 cm^{-1}, unreacted $AlCl_3$ present in products containing more than $4AlCl_3$ per $B_{10}H_{10}^{2-}$ cannot be detected with a great sensitivity.

The frequency of the BH and AlCl vibrations are nearly the same for the four salts, but the bands observed with the alkaline salts are much broader than with the tetraalkylammonium salts.

The ^{27}Al NMR data (Table 1) show that the spectra contain only one peak for ratios not exceeding 4:1. The second peak appearing for a higher $AlCl_3$ content is obviously due to $AlCl_3$ itself. The position of the main peak is very close to that of $AlCl_4^-$ and $Al_2Cl_7^-$ obtained by reaction of Et_4NCl with $AlCl_3$. In both cases the peaks are broadened when the $AlCl_3$ content increases.

Solid NMR of the ^{11}B nucleus has not given significant results to allow us to elucidate the structure of the products. Using $B(OMe)_3$ as reference, two sharp peaks with an approximate ratio of 1:4 appear at $\delta = -19.95$ and -47.17 ppm on a broad peak. When the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio increases the broad peak having a half height width of approximately 125 ppm, centered at −38 ppm, becomes more intense while the sharp peaks disappear. Such a broad peak seems to indicate a strong interaction of the cage with the surrounding moieties [10].

Discussion

Many properties of $B_{10}H_{10}^{2-}$ substitution derivatives show that this anion forms a strongly electron donating ligand [4]. In the reaction with $AlCl_3$, it seems very probable that the boron anions coordinate aluminium, but various modes of coordination can be envisaged. The ^{27}Al NMR and IR data for Et_4NAlCl_4 and $Et_4NAl_2Cl_7$ are so close to those obtained for $(Et_4N)_2B_{10}H_{10}$–$AlCl_3$ mixtures that there is, at least, a strong analogy between the aluminium compounds present in both cases. From these considerations two interpretations of the experimental data have been proposed: (i) a pathway leading to the formation of $AlCl_4^-$ and $Al_2Cl_7^-$, and (ii) the association of $AlCl_3$ with the cage giving complexes of general formula $(B_{10}H_{10}, nAlCl_3)^{2-}$.

Complexes formed from $AlCl_3$ and various Lewis bases including CH_3COCl_3 [11], Et_2O [7], Me_2O, MeCN, HCO_2Me [12] and THF [8, 13] have been extensively studied owing to their interest in Friedel–Crafts reactions. These complexations give molecular compounds as well as ionic compounds. Concerning ionic type complexes, excluding a controversial example [5, 12], the anionic species is always $AlCl_4^-$. When there is no chloride capable of giving Cl^-, $AlCl_4^-$ is formed by disproportionation of $AlCl_3$. The cation produced is always complexed with the base: the solid complex of general formula $AlCl_3 \cdot 2THF$ corresponds [8] to the ionic arrangement $AlCl_4^- \cdot AlCl_2(THF)^+$ and the complex $AlCl_3 \cdot 1.5MeCN$ exists [12] as $Al(MeCN)_6^{3+},(AlCl_4^-)_3$. The $AlCl_2^+$ cation complexed with THF shows strong IR absorption at 457 cm^{-1} assigned to the $AlCl_2$ asymmetrical stretching vibration, and in a THF solution, an ^{27}Al NMR peak at 9 ppm with $Al(H_2O)^{3+}$ as reference. In the reaction of $AlCl_3$ with hydroborates, the presence of an $AlCl_2^+$ species with $AlCl_4^-$ and in a 1:1 ratio seems improbable, because there is no strong IR absorption near 460 cm^{-1} and the ^{27}Al NMR spectra exhibit only one peak at 99.1 ppm. Finally Al^{3+} is the only cation whose presence could be partly explained. The absence of an NMR peak which could be assigned to Al^{3+} remains an unresolved question, even if the cation were in a low concentration, and the bonds established with the boron cage could cause a broadening of the peak. During the reaction, the formation of $(AlCl_4^-)_3Al^{3+}$ should occur until the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio reaches 2:1. Further addition of $AlCl_3$ could be used for the easy conversion of $AlCl_4^-$ to $Al_2Cl_7^-$.

The other interpretation supposes that $AlCl_3$ units associate with $B_{10}H_{10}^{2-}$ without disproportionation. The IR data would imply a charge distribution with a negative charge localized in the vicinity of the $AlCl_3$ group. Thus, the addition of one or two $AlCl_3$ units of the cage (Fig. 3) should produce the equivalent of $AlCl_3Z^-$ entitites. This scheme supposes for the $B_{10}H_{10}^{2-}$ cage a great ability to release electrons but its chemistry gives evidence of such a property: the amine derivative $B_{10}H_8(NH_2)^{2-}$ is extremely basic and the carboxylic acid $B_{10}H_8(COOH)_2^{2-}$ is weak [14]. A study of its closely related B_{12} analog [15] has shown that each carbonyl group behaves in an insulated fashion as though its proton ionization were being effected by one negative charge. During the reaction, when the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio increases from 2 to 4, $AlCl_3$ is assumed to have the same behaviour with $AlCl_3Z^-$ as with $AlCl_4^-$ [16, 17], the Al atoms being bonded through a bent Al–Cl–Al bridge (Fig. 3).

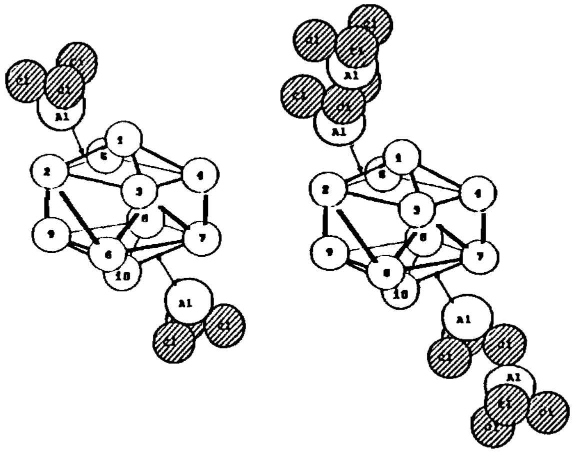

Fig. 3. Possible structure for $[B_{10}H_{10}(AlCl_3)]_2^-$ and $[B_{10}H_{10}(Al_2Cl_6)_2]^{2-}$. The hydrogen atoms have been omitted.

The aluminium-cage interactions can be examined in the same manner whether a disproportionation takes place or not. Only one bond would be created with $AlCl_3$ whereas Al^{3+} would require several bonds to stabilize the system. The chemistry of aluminoboranes shows that Al can be bonded to the cage through three centre B–H–Al bridge bonds or by coordination to boron boron bonds [18–21]. Structural studies on $Cu_2B_{10}H_{10}$ [22–24] which has a covalent character or its analogue in which copper(I) is complexed with triphenyl phosphine [25] suggest that one should consider the two previous types of bonds which could be interfering. Beside the terminal BH bands between 2510 and 2570 cm^{-1}, the IR spectrum of $Cu_2B_{10}H_{10}$ contains a broad band at 2100–2300 cm^{-1} which suggests some Cu–H–B interaction. Similarly with $(Ph_3)_2CuB_{10}H_{10}Cu(Ph_3)_2$ two broad bands at 2230 and 2335 cm^{-1} are assigned to CuHB stretching modes. In the reaction of $AlCl_3$ with $B_{10}H_{10}^{2-}$ the IR spectra for ratios of $AlCl_3$ to

$B_{10}H_{10}^{2-}$ exceeding 2, contain two medium intensity bands at 2342 and 2430 cm^{-1}. This could indicate some B–H–Al interaction but this interaction should be very weak because compared to the BH vibrations the frequency shift is low.

There are many examples of metallic atoms bonded to a boron cage by coordination to a B–B bond [26]. The formation of three centre B–Al–B bonds through this mechanism would account for the cage electron donation to the aluminium atom because B–B bonds act as if they possess excess electron density and function as electron donors to Lewis acids [27]. A possible structure for the $B_{10}H_{10}^{2-}$,2$AlCl_3$ and $B_{10}H_{10}^{2-}$,4$AlCl_3$ derivatives is shown in Fig. 3. $AlCl_3$ has been supposed to coordinate the B_1 B_2 and B_7 B_{10} bonds because three centre B–H–B bonds are probably established in these positions (or equivalent positions) when a proton attacks the cage [28, 29].

The probability of the two patterns accounting for the data obtained does not seem to be the same. The positions of the ^{27}Al NMR peak observed for Et_4NAlCl_4 and $AlCl_3$–$B_{10}H_{10}^{2-}$ mixtures are identical within experimental error. This suggests that $AlCl_4^-$ is present in both cases. However, the chemical shift does not seem to be greatly affected by the exchange of a chlorine atom of $AlCl_4^-$ for another ligand since in solution a change of only 4 ppm occurs when a chlorine atom is substituted for a bromine atom [30]. The fact that no significant variation of the chemical shift was observed when $AlCl_4^-$ was converted into $Al_2Cl_7^-$ is also consistent with the discussion above. As previously mentioned, the absence of an ^{27}Al NMR peak attributable to a cationic species suggests that there is no formation of $AlCl_4^-$.

The IR spectra for $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratios of 2:1 have been compared to those of $AlCl_4^-$ and $AlCl_3Br^-$ [31]. For an $AlCl_4^-$ anion having tetrahedral symmetry, there is only one IR active vibration in the 300–600 cm^{-1} region. This vibration which is the triply degenerate $AlCl_4^-$ stretching vibration ν_3 gives a strong absorption at 490 cm^{-1} generally with shoulders on both sides. When the $AlCl_4^-$ tetrahedron is perturbed structurally [32–34], the ν_1 $AlCl_4^-$ stretching vibration of symmetry A_1 which is Raman active appears in IR at 350–353 cm^{-1} giving a weak or very weak band. The IR spectrum of $AlCl_3Br^-$ of C_{2v} symmetry contains a strong band at 495 cm^{-1} (ν_4), a strong band at 308 cm^{-1} (ν_2) and another IR active band ν_1 with a calculated frequency of 440 cm^{-1}. The IR spectrum shown in Fig. 2b contains a strong absorption at 492 cm^{-1}, a band of medium intensity at 335 cm^{-1} and perhaps a weak band near 425 cm^{-1}. A comparison between various MX_3Z molecules [35] shows that the frequency of ν_2, the MZ stretching vibration, depends upon the nature of Z. Due to its intensity and its position, the band at 335 cm^{-1} seems more likely to be due to a $AlCl_3Z^-$ system than to $AlCl_4^-$.

Two general considerations should also be mentioned: (i) the observed stoichiometry of 2:1 coincides with the number of negative charges required for the formation of $AlCl_3Z^-$ whereas the disproportionation of $AlCl_3$ leading to $AlCl_4^-$ and Al^{3+} bonded to the cage should be limited only by steric hindrance; (ii) BH stretching vibrations are modified when the $AlCl_3$ to $B_{10}H_{10}^{2-}$ ratio increases from 2 to 4. This effect is more compatible with the addition of $AlCl_3$ to $AlCl_3$ groups attached to the cage than the same addition on independent $AlCl_4^-$. At this stage of the study, a disproportionation reaction accompanied by the formation of ions seems less probable than a simple interaction involving a new distribution of charges. The possibility for a Lewis acid to react with a closohydroborate is certainly related to the ability of the cage to release electrons. New reactions of the same type will be investigated.

Caution: Reactions of $(Et_4N)_2B_{10}H_{10}$ and $K_2B_{10}H_{10}$ with $AlCl_3$ in liquid SO_2 after evaporation of the solvent give a solid product which is hazardous to handle. This product generally explodes when it is crushed. According to its IR spectrum it contains a mixture of the hydroborate and the $AlCl_3SO_2$ complex.

Experimental

$(Et_4N)_2B_{10}H_{10}$ was prepared according to published methods [36, 37]; $K_2B_{10}H_{10}$ and $Na_2B_{10}H_{10}$ were obtained from $(Et_4N)_2B_{10}H_{10}$ by ion exchange on a C 20 Duolite resin. Solid $(Bu_4N)_2B_{10}H_{10}$ was prepared by addition of Bu_4NCl to an aqueous solution of $K_2B_{10}H_{10}$. The salts were dried at 0.05 Pa and 120 °C for at least 24 h before use. $AlCl_3$ (Merck) was purified by repeated sublimation *in vacuo*. The manipulations and reactions were carried out in a glove box filled with perfectly dry argon and continuously purified by means of a gas circulation device.

In a typical reaction a suspension of 0.4 g of $(Et_4N)_2B_{10}H_{10}$ (or the equivalent amount of another salt) and a suitable mass of $AlCl_3$ was stirred in refluxing hexane for 12 h. After this time (or for 10 h more with alkaline salts), the IR spectrum of the product had ceased to change. The solid was recovered by filtration. No product dissolved in hexane when the reaction was carried out in anhydrous conditions. The same reaction performed with hydrated $AlCl_3$ gave a hexane solution of 6-$B_{10}H_{13}Cl$ with occasional traces of $B_{10}H_{14}$ as impurity. With $(E_4N)_2B_{10}H_{10}$, the chlorodecaborane can be obtained in a yield exceeding 45% when $AlCl_3$ is used in a large excess.

Et_4NAlCl_4 and $Et_4NAl_2Cl_7$ were prepared from Et_4NCl and $AlCl_3$ according to the same method as for the boron–aluminium compounds.

The IR spectra of the solid were recorded as nujol mulls in an hermetic cell with CsI windows on a 457 Perkin-Elmer instrument. We have reported the IR data (in cm^{-1}) for several mixtures.

$AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ in a 2:1 ratio: 2545s, 2430w, 2342w, 1185m, 1170w, 1080w, 1035m, 1007m, 795m, 670w, 574w, 492s, 335m.

$AlCl_3$–$(Et_4N)_2B_{10}H_{10}$ in a 4:1 ratio: 2570s, 2430m, 2340m, 1185s, 1170m, 1100m, 1080w, 1005s, 955w, 875w, 830w, 792s, 680s, 550s, 492s, 385m, 332s.

$AlCl_3$–$(Bu_4N)_2B_{10}H_{10}$ in a 4:1 ratio: 2560s, 2428m, 2242m, 1170w, 1150w, 1107w, 1030w, 990w, 955w, 870m, 835m, 800m, 740m, 682m, 552s, 495s, 435w, 385m, 335m.

$AlCl_3$–$K_2B_{10}H_{10}$ in a 10:1 ratio: 2560m, 2450w, 2415w, 2320w, 1170w, 1035w, 1000w, 785m, 687m, 490w, 328s.

$AlCl_3$–$Na_2B_{10}H_{10}$ in a 10:1 ratio: 2565m, 2450w, 2320vw, 1165w, 1085vw, 685vw, 600m, 490s, 335s.

^{27}Al and ^{11}B NMR spectra were obtained at 96.25 MHz on a Bruker model MSL 300 spectrometer equipped with a M.A.S. head. The sample was placed into a rotor made of zirconia and tightly closed. The rotor was spinning at about 4 KHz. The number of accumulations was 100 to 1000.

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