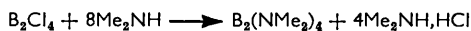


654. The Reactions of Diboron Tetrachloride with Some Nitrogen-containing Donor Molecules.

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The adducts $2D, B_2Cl_4$ are formed by direct reaction of diboron tetrachloride with $D = Me_3N, C_5H_5N, MeCN,$ and HCN ; these are involatile and thermally stable and do not react with olefins. Addition of hydrogen chloride can give diborates, *e.g.*, $[Me_3NH]_2[B_2Cl_4]$, and the methyl cyanide adduct adds trimethylamine with only partial displacement of the cyanide, suggesting formation of $[Me_4N]_2[B_2Cl_4(CN)_2]$. With $D = (CH_2 \cdot NMe_2)_2$, a 1 : 1 adduct is formed which is polymeric; with $D = N_2H_4, NH_2 \cdot NMe_2,$ and $(CH_2 \cdot NH_2)_2$, elimination of hydrogen chloride as the hydrochloride follows donation and polymeric B-N compounds containing boron-boron bonds are formed. $D = Me_2NH$ gives a mixture of $B(NMe_2)_3, B_2(NMe_2)_4,$ and polymeric $BNMe_2$.

PREVIOUS studies of the reactions of diboron tetrachloride with ammonia and amines¹ and with cyanogen² have shown that both boron atoms act as acceptors, giving 2 : 1 adducts. When the donor molecule contains reactive hydrogen, elimination of hydrogen chloride as the hydrochloride of the donor base follows, *e.g.*:¹



We now report the reactions of diboron tetrachloride with both mono- and bi-dentate nitrogen-donor molecules.

EXPERIMENTAL

Diboron tetrachloride was prepared and purified as previously described.³ Donor substances were prepared (where necessary) by conventional methods and purified by fractionation in the vacuum-system. In a typical reaction, measured amounts of diboron tetrachloride and the donor were mixed at liquid-nitrogen temperature and the mixture was allowed to warm until reaction was observed (usually at the m. p. of the donor); the reaction temperature was kept as low as possible to minimise decomposition of the unchanged diboron tetrachloride. Decomposition was, however, often catalysed by the donor, and hence precise reaction ratios could not always be observed. When reaction was complete, the excess of donor was removed and measured, together with any volatile products which were separated and identified. The reaction product was examined (*a*) by hydrolysis in a sealed tube (evolved hydrogen and chloride ion were determined, but accurate boron determinations were usually nullified by interference of the donor base in the titrations), (*b*) by heating it in a sealed tube, volatile products being removed as before, (*c*) by addition of ethylene or but-2-ene, and (*d*) by addition of hydrogen chloride or trimethylamine. The decomposition of diboron tetrachloride during reaction with a donor yielded boron trichloride and polymeric BCl , the latter being red or yellow; separate experiments indicated that the rate of reaction of $(BCl)_n$ with a donor was negligibly slow under the conditions used. Hence the main product was contaminated with small amounts of the donor-boron trichloride adduct and with $(BCl)_n$. Reaction of an excess

¹ Urry, Wartik, Moore, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5293.

² Apple and Wartik, *J. Amer. Chem. Soc.*, 1958, **80**, 6158.

³ Holliday and Massey, *J.*, 1960, 43.

of diboron tetrachloride with a donor appeared to yield the same product as when an excess of donor was used, the unchanged tetrachloride forming more trichloride and $(\text{BCl})_n$; such reactions were not, therefore, studied in detail. The amount of reaction product in an experiment was usually 0.5–1.0 mmole.

RESULTS AND DISCUSSION

The results are summarised in the Table. The quoted reaction ratios represent the mean of at least two (usually four) determinations, except that for hydrogen cyanide which is the value of a single observation. The donors listed in the top part of the Table each gave only a solid adduct with no other products; in the lower part, elimination of hydrogen chloride as the donor hydrochloride occurred.

Trimethylamine.—The adduct $2\text{NMe}_3\cdot\text{B}_2\text{Cl}_4$ was formed readily as a white solid. In the previously reported preparation¹ a sublimate from the adduct was soluble in benzene and gave a cryoscopic molecular weight corresponding to $[(\text{NMe}_3)_2\text{B}_2\text{Cl}_4]_4$. Our specimen was almost insoluble in benzene (0.3%) and molecular-weight determinations were insufficiently precise to have meaning. Almost quantitative 2:1 addition of hydrogen chloride to the adduct occurred slowly, without evolution of any volatile product other than a trace of hydrogen; there was no evidence for the formation of diboron tetrachloride or its decomposition products. A similar addition of hydrogen chloride to the adducts

Donor (D)	Reaction ratio (D : B_2Cl_4)	Products	Thermal stability	Hydrolysis products (%)		Addition per mole of adduct	
				H_2	Cl	HCl	NMe_3
Me_3N	1.92	Solid adduct	High	—	—	1.92	—
$\text{C}_2\text{H}_5\text{N}$	1.98	"	"	46	99.5	0.25	—
MeCN	1.95	"	Decomp. <130°	90	98	—	1.95
HCN	1.92	"	—	—	—	—	—
$(\text{CH}_3\cdot\text{NMe}_2)_2$	1.06	"	High	82	98	0.55	—
N_2H_4	4.9	$(\text{B}_2\text{N}_2)_n + \text{HCl}$	—	30–55	—	—	—
$\text{NH}_2\cdot\text{NMe}_2$	3.05	$(\text{BClNMe})_n + \text{HCl}$	—	2–55	—	—	—
$(\text{CH}_3\cdot\text{NH}_2)_2$	5.07	$[\text{B}_2\text{N}_2(\text{CH}_3)_2]_n + \text{HCl}$	—	90	—	—	—
Me_2NH	7.32	$\text{B}(\text{NMe}_2)_3, \text{B}_2(\text{NMe}_2)_4,$ $(\text{BNMe}_2)_n + \text{HCl}$	—	—	—	—	—

$2\text{Me}_3\text{N}\cdot\text{Cl}_2\text{B}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{BCl}_2$ (R = H or Me) has been attributed to formation of compounds $[\text{Me}_3\text{NH}]_2[\text{Cl}_3\text{B}\cdot\text{CHR}\cdot\text{CHR}\cdot\text{BCl}_3]$ ^{3,4} and formation of a hexachlorodiborate $[\text{Me}_3\text{NH}]_2[\text{B}_2\text{Cl}_6]$ is probable here; hydrolysis after addition of the hydrogen chloride indicated no loss of boron–boron bonding. Evidence for the formation of the $[\text{B}_2\text{Cl}_6]^{2-}$ ion has been obtained in the titration of diboron tetrachloride with tetramethylammonium chloride in anhydrous hydrogen chloride as solvent.⁵ The trimethylamine–diboron tetrachloride adduct did not react with ethylene.

Pyridine.—The adduct $2\text{py}\cdot\text{B}_2\text{Cl}_4$ was formed by a vigorous reaction which occurred when the mixture was warmed to the melting point of pyridine; a yellow coloration suggested formation of some $(\text{BCl})_n$. Hydrolysis of the adduct gave a very low yield of hydrogen, either because B–B bonding had been lost by some intramolecular rearrangement or because reduction of the pyridine rings occurred on hydrolysis [formation of any $\text{py}\cdot\text{BCl}_3$ requires formation of an equal amount of (BCl) which yields hydrogen on hydrolysis; hence the low hydrogen figure could not be due to decomposition of the tetrachloride]. When the adduct was heated to $\sim 200^\circ$, there were no volatile products (other than a trace of pyridine probably occluded in the adduct) and no change in appearance, but the hydrogen yield on hydrolysis had fallen to 16%. Uptake of hydrogen chloride by the adduct was apparently incomplete even after 40 hours' heating at 100° and did not approach the 2 mol. expected for a pyridine adduct, where formation of a dipyridinium hexachlorodiborate might be expected. These observations suggest that

⁴ Feeney, Holliday, and Marsden, *J.*, 1961, 356.

⁵ Holliday, Peach, and Waddington, *Proc. Chem. Soc.*, 1961, 220.

some rearrangement of the adduct occurs on formation and is taken further on heating; it is to be noted that the pyridine-boron trichloride adduct may well have a structure $[\text{py}_2\text{BCl}_2][\text{BCl}_4]$,⁶ and some similar structure may obtain for the rearranged tetrachloride adduct. There was no reaction of the adduct with ethylene.

Methyl Cyanide and Hydrogen Cyanide.—Since addition to diboron tetrachloride can occur by π -donation,^{7,8} there was the possibility of 1 : 1 addition of either of these donors through the C-N π -bond. The observed reaction ratio was 2 : 1 (even when excess of the tetrachloride was used), and only traces of other volatile products were formed; one of these was hydrogen chloride; the others were not identified. Reaction of hydrogen chloride with methyl cyanide to give 1,1-dichloroethylamine⁹ did not occur under the conditions used in our experiments. There was less evidence of decomposition of the tetrachloride when the methyl cyanide adduct was formed than in other donor reactions. The adduct $2\text{MeCN}, \text{B}_2\text{Cl}_4$ was more rapidly hydrolysed than the trimethylamine or pyridine adducts, and the hydrogen recovery indicated that B-B bonding was retained. The adduct was also less stable thermally, and heating at 130° for some hours gave a sublimate of methyl cyanide-boron trichloride with small amounts of free methyl cyanide and a residue having the characteristic yellow colour of $(\text{BCl})_n$. This result clearly suggests dissociation of the adduct on heating, the liberated cyanide then combining with the boron trichloride which would be formed rapidly from the tetrachloride at 130°. The stability of the tetrachloride adduct was sufficient to prevent reaction with ethylene, which did not occur even after many days at 20°. However, trimethylamine reacted readily at 20° and 2 mol. were taken up, suggesting complete displacement of the cyanide. Unexpectedly, the amount of methyl cyanide recovered was much less than 2 mol.—the average recovery from four experiments was 50%. Also, the remaining solid became orange-red in contact with the trimethylamine, and the same colour was observed if less than 2 mol. of trimethylamine were added to 1 mol. of the cyanide adduct. When methyl cyanide was added to the white trimethylamine adduct $2\text{Me}_3\text{N}, \text{B}_2\text{Cl}_4$, uptake of some cyanide and a colour change to orange-red occurred slowly on storage. Hydrolysis of the adduct $2\text{MeCN}, \text{B}_2\text{Cl}_4$ to which trimethylamine had been added gave a 75% recovery of hydrogen on hydrolysis, compared with 90% from the original adduct. The infrared spectrum of the red solid formed when trimethylamine was added showed absorption peaks similar to those observed for trimethylamine-diboron tetrachloride, together with some additional peaks which could not be assigned.

These observations suggest that displacement of methyl cyanide by trimethylamine occurs to a limited extent, but that fission of co-ordinated methyl cyanide also occurs to form a quaternary dicyanodiborate, analogous to the hexachlorodiborate:



Hydrogen cyanide formed a white solid $2\text{HCN}, \text{B}_2\text{Cl}_4$ similar to the methyl cyanide adduct. When hydrogen cyanide was kept in contact with the trimethylamine-diboron tetrachloride adduct for some hours, first at 20° and then at 100°, 1.8 mol. of hydrogen cyanide were taken up per mol. of adduct without evolution of trimethylamine or other volatile product, and again the solid became red, again suggesting formation of the compound $[\text{Me}_3\text{NH}]_2[\text{B}_2\text{Cl}_4(\text{CN})_2]$. As further evidence, the white 1 : 1 adduct $\text{MeCN}, \text{BCl}_3$ was prepared by direct addition *in vacuo*,¹⁰ and on addition of excess of trimethylamine 1 mol. was gradually taken up and only 5% of the theoretical amount of methyl cyanide liberated, the colour becoming orange-red. Here also the predominant reaction is the formation of a cyano-trichloroborate $[\text{NMe}_4][\text{BCl}_3(\text{CN})]$, and the colour appears to be a property associated with anionic B-CN bonding and not with the B-B bond.

⁶ Greenwood and Wade, *J.*, 1960, 1130.

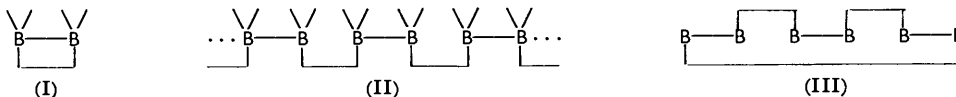
⁷ Holliday, Massey, and Taylor, *Proc. Chem. Soc.*, 1960, 359.

⁸ Holliday and Massey, *J. Inorg. Nuclear Chem.*, 1961, 18, 108.

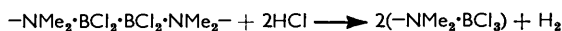
⁹ Hinkel and Treharne, *J.*, 1954, 866.

¹⁰ Laubengayer and Sears, *J. Amer. Chem. Soc.*, 1945, 67, 164.

NNN'N'-*Tetramethylethylenediamine*.—Reaction of a bidentate donor with diboron tetrachloride is of interest because co-ordination ring may occur with a single molecule (I) or by linking molecules (II) with the possibility of ring formation (III). A vigorous reaction



with the diamine (tmen) occurred at the melting point of the latter; it was difficult to remove all the unchanged diamine from the white solid product, but the reaction ratio was sufficiently close to 1 : 1 to indicate donation by both nitrogen atoms. A trace of volatile white solid too small for identification was removed with the unchanged amine, but the bulk of the product was involatile and insoluble in benzene, suggesting a structure of type (II) or (III) rather than (I). Hydrolysis gave slow but quantitative recovery of chloride and the hydrogen yield indicated that most of the B-B bonding was retained in the adduct. Reaction with hydrogen chloride was also slow, and after many hours at 20°, followed by heating, only about half a mol. per mol. of adduct was taken up. The only volatile product was a small amount of hydrogen, and there was no evidence of free diboron tetrachloride or its decomposition products. Hydrolysis yielded all the chlorine as chloride, and the hydrogen yield was 73%, only a small decrease compared with the original adduct. Reaction of an adduct of type (I) with hydrogen chloride to give [tmenH₂][B₂Cl₆] seems feasible; reaction with a compound of type (II), which might be highly polymerised, could be less easy; moreover, attack on such a structure might be as likely at the B-B as at the B-N bonds, *i.e.*, the reaction



could occur. The evidence is therefore again in favour of the structure (II), with some reaction to give a diborate but also slight attack on the B-B bonding to give hydrogen, with consequent loss of the latter on hydrolysis. An attempt to convert the original adduct into the boron trichloride adduct, by attacking the B-B bond with chlorine, was unsuccessful; only slight uptake of chlorine occurred, and the simultaneous liberation of hydrogen chloride indicated attack on the methylene groups rather than on the B-B bonds. No boron trichloride adduct could be identified in the product.

Hydrazine and NN-Dimethylhydrazine.—The reaction ratio 5 for addition of hydrazine indicated initial donation by both nitrogen atoms, followed by elimination of 4 mol. of hydrogen chloride as hydrazine hydrochloride, *i.e.*:



With the dimethylhydrazine, elimination of only two mol. of hydrogen chloride could occur, giving the observed ratio 3 : 1; the reactions are generally similar to those observed by Nöth¹¹ between alkyl- and aryl-boron halides and hydrazines, in which, *e.g.*, a compound R_{3-n}BCl_n reacted with (n + ½) mol. of hydrazine with formation of the hydrochloride. With either hydrazine or dimethylhydrazine, the products were white involatile solids and could not be separated from the hydrochlorides. With hydrazine other reactions could also occur easily; in some experiments the diboron tetrachloride appeared to initiate violent and complete decomposition before addition, giving nitrogen and hydrogen (dimethylhydrazine also yielded methane), while in other experiments much initial decomposition of the tetrachloride occurred. Hydrolysis of the solid products of normal reactions gave very variable amounts of hydrogen, these being always much lower than theoretical; the simultaneous formation of ammonia (from the hydrazine reaction) and dimethylamine (from dimethylhydrazine) indicated reduction of the hydrochlorides. Hence it seems probable that B-B bonding did remain in the products to a considerable extent, and that

¹¹ Nöth, 17th Internat. Congress Pure Appl. Chem., Munich, 1959.

these should be formulated with $-N-B-B-N-N-B-B-N-$ chains rather than with chains containing alternate boron and nitrogen atoms.

Ethylenediamine.—This reaction followed a similar course to the hydrazine addition, with a 5 : 1 reaction ratio and a white solid product which on hydrolysis (with hydrochloride still present) gave a high recovery of hydrogen, indicating retention of B-B bonding and little reduction of the hydrochloride.

Dimethylamine.—A previous study¹ of the reaction with diboron tetrachloride gave a reaction ratio of less than 8 : 1 with tetrakis(dimethylamino)diboron as the chief product, tris(dimethylamino)borine also being formed in small amounts. The properties of the diboron compound, $B_2(NMe_2)_4$, have since been studied in more detail.¹² Of all the reactions described in this paper this was the only one to give substantial amounts of volatile products. Reaction was very slow at -78° and even after a long time at 20° less than 8 mol. of the dimethylamine had reacted. The incompleteness of reaction may be due to the very slow reaction of the intermediate $Me_2N \cdot BCl_2 \cdot BCl_2 \cdot NMe_2$ with more amine, since this intermediate did not react with dimethylaminodimethylborine⁷ to give the tetra-aminoboron. After removal of the excess of dimethylamine, the volatile products were hydrolysed, and the low hydrogen evolution indicated presence of some substance not containing B-B bonds. The B : $NHMe_2$ ratio in the hydrolysate showed that $B_2(NMe_2)_4$ and $B(NMe_2)_3$ were present in the volatile fraction in approximately equimolar amounts, and this was confirmed by examination of the infrared spectrum of the fraction. Since the aminodiboron has high thermal stability¹² it is unlikely that the aminoborine could have been formed from it. There was little evidence that the diboron tetrachloride had decomposed to the extent required to provide enough boron trichloride to react with dimethylamine and form the aminoborine: some coloration due to $(BCl)_n$ was observed but this remained throughout the reaction period. It is possible that, at the stage where one dimethylamine molecule had co-ordinated and one molecule of hydrogen chloride had been eliminated to give $Me_2N \cdot BCl_2 \cdot BCl_2$, disproportionation of the latter to boron trichloride and $(Me_2NB)_n$ might occur, with subsequent formation of the aminoborine from the trichloride, the $(Me_2NB)_n$ remaining as a solid residue. It is to be noted that certain secondary amines can effect disproportionation of boron trichloride.¹³

The results with the various donors indicate that both boron atoms in the tetrachloride have strong acceptor power, qualitatively comparable to that of boron trichloride, and there is no tendency for donation to the second boron atom to be diminished by prior donation to the first. The general stability of the adducts and the lack of reactivity towards olefins further support the idea that the reactivity of diboron tetrachloride and its ability to react with olefins are attributable to the presence of vacant orbitals on adjacent bonded atoms rather than to inherent weakness of the B-B bond.

Grants from the Department of Scientific and Industrial Research are acknowledged by F. J. M. and A. G. M.

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[Received, March 2nd, 1961.]

¹² Brotherton, McCloskey, Petterson, and Steinberg, *J. Amer. Chem. Soc.*, 1960, **82**, 6242.

¹³ Gerrard, Hudson, and Mooney, *J.*, 1960, 5169.