Lewis Acidity of Dodecafluoro-octaborane(12) and Trifluorophosphine–tris(difluoroboryl)borane (1/1): A Nuclear Magnetic Resonance Study of Reactions with Trimethylamine

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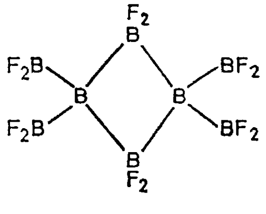
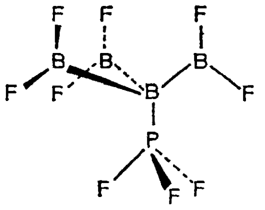
Low-temperature n.m.r. studies of the $Me_3N + F_3P\cdot B(BF_2)_3$ system indicate the formation of adducts $F_3P\cdot B(BF_2NMe_3)_n(BF_2)_{3-n}$ ($n = 1$—3). The compound B_8F_{12} is very reactive toward Me_3N in dichloromethane solution at −90 °C and the only product tentatively identified is $Me_3N\cdot B(BF_2)_3$.

DODECAFLUORO-OCTABORANE(12), B_8F_{12}, is the best known of the higher boron fluorides and appears to have the structure (I).[1] It reacts with donor molecules of the type classified as ' soft bases '[2] to form thermally stable complexes of structure $D\cdot B(BF_2)_3$. The crystal structure of the PF_3 complex, (II), has been determined.[3] However, with ' hard bases '[2] such as Me_3N rapid decomposition of B_8F_{12} occurs even at −70 °C, and the only products which have been isolated are the BF_3 complexes of the donor molecules.[1]



(I)



(II)

We have now studied the reaction of Me_3N with the BF_2 groups of $F_3P\cdot B(BF_2)_3$, a complex in which the ' super-acid '[1] central electron-pair acceptor site is protected by an especially stable donor–acceptor linkage. We have also investigated the reaction between Me_3N and B_8F_{12} in solution at −90 °C in an attempt to detect the initially formed complex.

EXPERIMENTAL

Dodecafluoro-octaborane(12) and trifluorophosphine–tris(difluoroboryl)borane (1/1) were prepared as described previously.[1] Trimethylamine was dried over calcium hydride before use. Dichloromethane was dried over calcium sulphate, followed by drying over P_2O_5, before use. N.m.r. samples were made up and sealed off using standard high-vacuum techniques.

Proton and fluorine-19 n.m.r. spectra were obtained on a Varian Associates HA 100 spectrometer operating at 100 and 94·1 MHz respectively. Boron-11 spectra were obtained on a Bruker WH 90 Fourier-transform spectrometer operating at 28·87 MHz. Proton chemical shifts are given in p.p.m. to low field of external tetramethylsilane. Fluorine-19 and boron-11 chemical shifts are given in p.p.m. to high field of external trichlorofluoromethane and external $Et_2O\cdot BF_3$ respectively. The adduct $F_3P\cdot B(BF_2)_3$ dissolved readily in dichloromethane at room temperature; ^{19}F and ^{11}B n.m.r. parameters are similar to those observed in $CFCl_3$.[1] The compound is insoluble at −90 °C, but goes into solution as Me_3N adducts in the presence of Me_3N. Bright yellow B_8F_{12} dissolved in dichloromethane at −90 °C to give a yellow-brown solution which was stable at temperatures up to *ca.* −50 °C and from which unchanged B_8F_{12} could be recovered by trap-to-trap distillation. The −90 °C ^{19}F n.m.r. spectrum consisted of a single major peak at 50·0 p.p.m. (pure liquid and solution in $CFCl_3$, 44·1 p.p.m.[1]). Small impurity peaks were also present at 121·7 (BF_3) and 37·9 p.p.m. Warming to −23 °C resulted in decomposition with rapid evolution of BF_3 and fading of colour over a few minutes.

RESULTS AND DISCUSSION

The Reaction of Me_3N *with* $F_3P\cdot B(BF_2)_3$.—Our ^{19}F, ^1H, and ^{11}B n.m.r. results are in accord with the following reaction scheme in which $F_3P\cdot B(BF_2)_3$, (II), acts as a three-site Lewis acid:

$$\begin{tikzcd} F_3P\cdot B(BF_2)_3 \arrow[r, "(i)"] & F_3P\cdot B(BF_2NMe_3)(BF_2)_2 \arrow[d, shift left, "(i)"] \\ F_3P\cdot B(BF_2NMe_3)_3 \arrow[r, shift left] & F_3P\cdot B(BF_2NMe_3)_2(BF_2) \arrow[l, shift left, "(ii)"'] \arrow[u, shift left] \end{tikzcd}$$

(*i*), Me_3N; (*ii*), excess of Me_3N

Two of the three BF_2 sites of (II) complex readily at −90 °C, but the third is less easily complexed. ^{19}F N.m.r. parameters of (II) and its adducts are given in the Table.

−90 °C ^{19}F N.m.r. parameters of $F_3P\cdot B(BF_2NMe_3)_n(BF_2)_{3-n}$ (n = 0—3)

n	0[a]	1	2	3
Chemical shift:[b]				
Free BF_2	39·4	43·5	41·9	
Complexed BF_2[c]		132·8	133·1	126·8 and 130·7
F_3P	52·3	53·3	51·0	45·6
$J(^{19}F–^{31}P)$/Hz	1 350	1 350	1 380	1 360

[a] −50 °C Spectrum; insoluble at −90 °C; lit.,[1] 37·4 (BF_2), 53·9 p.p.m. (F_3P). [b] P.p.m. to high field of external $CFCl_3$ in CH_2Cl_2 solution. [c] Broad resonances due to unresolved boron–fluorine coupling.

Low-temperature ^{19}F spectra of dichloromethane solutions of Me_3N and (II) of various mol ratios demonstrated

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[1] R. W. Kirk, D. L. Smith, W. Airey, and P. L. Timms, *J.C.S. Dalton*, 1972, 1392.

[2] R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 581, 643; *J. Amer. Chem. Soc.*, 1963, **85**, 3533.

[3] B. G. DeBoer, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 1969, **8**, 836.

the presence of all species in the series $F_3P{\cdot}B(BF_2NMe_3)_n(BF_2)_{3-n}$ ($n = 0$—3). The BF_2 resonances of (II) and its adducts were broad due to unresolved ^{11}B–^{19}F coupling. The large high-field shifts which occurred on complexing of successive BF_2 groups of (II) are consistent with the expected change from trigonal-planar to tetrahedral geometry at the BF_2 boron (*cf.* BF_2Br, 53 p.p.m.;[4] $Me_3N{\cdot}BF_2Br$, 134·0 p.p.m.[5]). Thus the $n = 1$ adduct was identified by its two low-temperature BF_2 resonances in a 2 : 1 ratio at 43·5 and 132·8 p.p.m. respectively. PF_3 Resonances were relatively sharp doublets due to ^{19}F–^{31}P coupling; on complexing of the first Me_3N, the doublet shifted slightly to higher field, but two further base molecules caused a marked low-field shift toward the value of uncomplexed PF_3 (35·1 p.p.m.[6]). Although the broad BF_2 resonances of the different adducts overlapped, the sharp PF_3 doublets could be clearly distinguished.

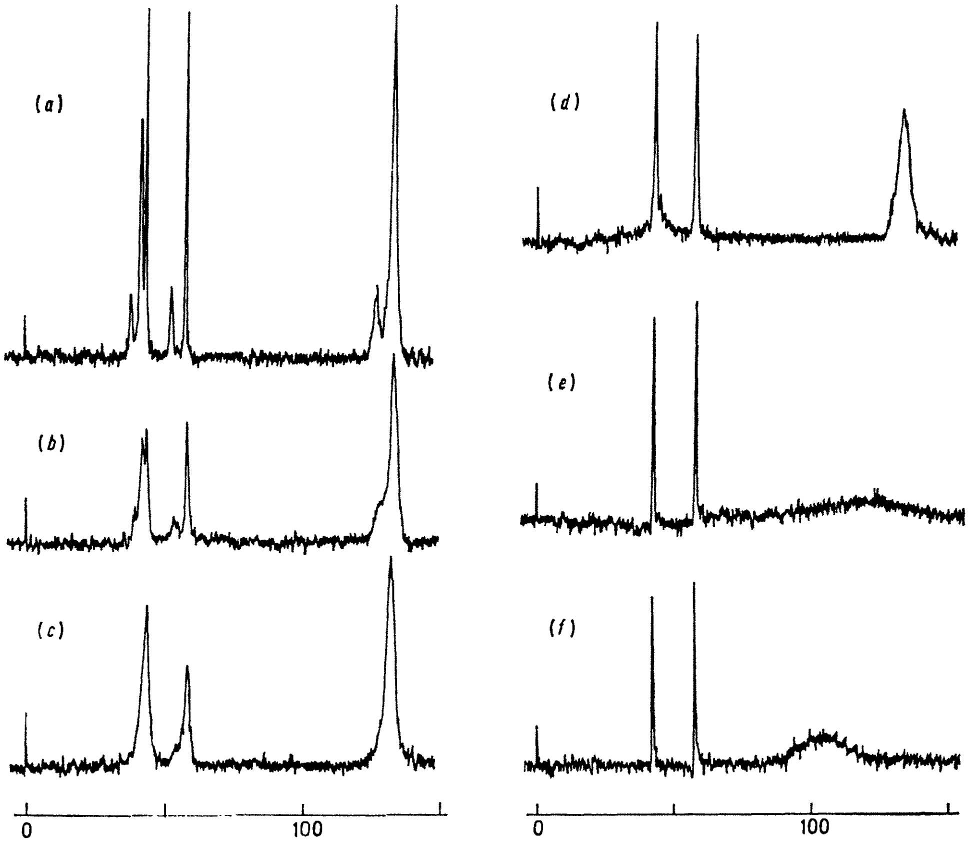

FIGURE 1 ^{19}F N.m.r. spectra of a $Me_3N + F_3P{\cdot}B(BF_2)_3$ solution of mol ratio 3 : 1 at −90 (*a*), −85 (*b*), −80 (*c*), −70 (*d*), −50 (*e*), and −20 °C (*f*). The adduct $F_3P{\cdot}B(BF_2NMe_3)_2(BF_2)$ is the predominant species

The $n = 1$ adduct is the most stable. Thus, while a freshly prepared −90 °C solution of Me_3N and (II) in a 1 : 1 mol ratio contained both $n = 1$ and 2 adducts and some insoluble uncomplexed (II), brief warming to 20 °C led to complete −90 °C solubility and a simpler −90 °C ^{19}F n.m.r. spectrum corresponding to the 1 : 1 adduct only. No further chemical-exchange effects could be detected in this sample up to room temperature once the initial reaction was complete. When the mol ratio of Me_3N to (II) was greater than 1 : 1, Me_3N exchanged rapidly and reversibly among the adducts. Thus coalescence of the ^{19}F n.m.r. peaks of the $n = 2$ and 3 adducts gave at −20 °C a single BF_2 resonance and a single PF_3 doublet (Figure 1). Exchange became more rapid as the Me_3N : (II) ratio increased. This is to be expected if the $n = 2$ and 3 adducts dissociate on warming, with the $n = 3$ adduct doing so the most readily. Complexing of two of the BF_2 sites greatly decreases the acidity of the third site and a large excess of Me_3N was required to shift the equilibrium to favour the $n = 3$ complex at −90 °C. Thus a 3 : 1 mol ratio of Me_3N to (II) gave mainly the $n = 2$ adduct (Figure 1). A 6 : 1 mol ratio gave *ca.* 93% of the $n = 3$ adduct at −90 °C, but dissociation became predominant at higher temperatures and the $n = 2$ adduct was the only major species at 20 °C.

At −90 °C the $n = 3$ adduct gave *two* complexed-BF ^{19}F n.m.r. peaks of different widths but of approximately equal areas. These peaks coalesced at *ca.* −85 °C

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[4] T. D. Coyle and F. G. A. Stone, *J. Chem. Phys.*, 1960, **32**, 1892.

[5] B. Benton-Jones, M. E. A. Davidson, J. S. Hartman, J. J. Klassen, and J. M. Miller, *J.C.S. Dalton*, 1972, 2603.

[6] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, 1962, **2**, 433.

(Figure 2). Their relative chemical shift (3·9 p.p.m.) was not much less than the relative chemical shift (5·2 p.p.m.) of the major and minor PF_3 doublets arising from the $n = 3$ and 2 adducts, yet the two complexed-BF peaks coalesced at a temperature *ca.* 50 °C lower than the two PF_3 doublets in the same sample. A different process, much faster than Me_3N exchange, must be responsible for the coalescence of the two complexed-BF peaks. The process being observed is probably restricted rotation about the boron–boron bonds. In (II) itself, each BF_2 group consists of an ' axial ' and an ' equatorial ' fluorine,[3] but separate ^{19}F resonances are not observed. Bulky Me_3N molecules would be expected to co-ordinate in ' equatorial ' positions, so that the preferred conformation of the 3 : 1 adduct would probably be as in (III), with equal amounts of ' axial ' and ' equatorial ' fluorines. It seems that only in the $n = 3$ adduct is rotation about the B–B bonds sufficiently hindered to be slow on the n.m.r. time scale, and even here the two peaks can be distinguished only at very low temperatures. The difference in peak widths (Figure 2) can be attributed to different ^{11}B–^{19}F coupling constants for the different fluorine orientations.

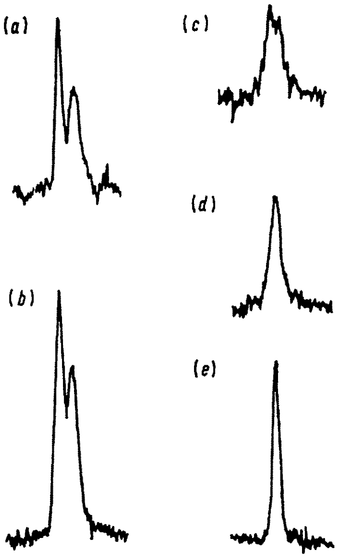
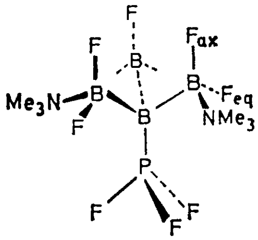


FIGURE 2 ^{19}F N.m.r. spectra of a $Me_3N + F_3P{\cdot}B(BF_2)_3$ solution of mol ratio 6 : 1, showing coalescence of the two complexed-BF peaks (126·8 and 130·7 p.p.m.) of $F_3P{\cdot}B(BF_2NMe_3)_3$, at −93 (*a*), −90 (*b*), −85 (*c*), −80 (*d*), and −70 °C (*e*)



(III)

^1H N.m.r. spectra confirmed that rapid Me_3N exchange occurs when excess of Me_3N is present. Trimethylamine complexed to (II) absorbed at 2·82 ± 0·02 p.p.m. to low field of external $SiMe_4$ at −90 °C (free Me_3N, 2·45 p.p.m.), and the chemical shift was little affected by the attachment of other molecules of Me_3N to the same molecule of (II). When the mol ratio of Me_3N to (II) was greater than 3 : 1, separate resonances of free and complexed Me_3N could be detected, but only at very low temperatures. The single peak observed at higher temperatures shifted closer to the free-Me_3N value as the temperature was raised, confirming the temperature-dependent dissociation of Me_3N. ^{11}B N.m.r. spectra provided further confirmation. When the mol ratio of Me_3N to (II) was 1 : 1, the expected three ^{11}B n.m.r. resonances in the ratio 2 : 1 : 1 were observed at room temperature, two of them (−34, +50 p.p.m.) being little changed in position from the peaks of uncomplexed (II) (BF_2 boron, −32 p.p.m.; central boron, +49 p.p.m.). The new resonance, a broad doublet at −7 p.p.m., is assigned to the complexed BF_2 group (*cf.* $Me_3N{\cdot}BF_2Cl$, −4·5 p.p.m.[7]). Samples containing an excess of Me_3N over (II) gave only two ^{11}B n.m.r. peaks, consistent with rapid chemical exchange of Me_3N among BF_2 sites. The chemical shift of the averaged BF_2 resonance moved closer to the free-BF_2 position as the temperature was raised, in accord with greater dissociation of Me_3N at higher temperatures. ^{31}P N.m.r. was not useful in this study because of large unresolved couplings to ^{11}B which gave peak widths of several KHz.

Further reactions occur in this system. Thus, whereas (II) alone is stable in dichloromethane well above room temperature, when Me_3N is present free PF_3 is slowly released (^{19}F doublet, 33·3 p.p.m.; lit.,[6] 35·1 p.p.m.) and $Me_3N{\cdot}BF_3$ is slowly formed. After 1 h at 40 °C a brown second liquid phase separated. It seems that even when PF_3 stabilizes the B_4 skeleton, Me_3N slowly breaks it down. An initial displacement of F_3P by Me_3N is likely, since this reaction is known to occur in the analogous $F_3P{\cdot}BH_3$ complex.[8] Additional products formed readily when there was insufficient Me_3N to complex in a 1 : 1 ratio with (II). Thus a freshly prepared solution of Me_3N and (II) in a 1 : 2 mol ratio contained a new species giving a broad −90 °C ^{19}F n.m.r. peak at 140·9 p.p.m., in addition to $F_3P{\cdot}B(BF_2NMe_3)(BF_2)_2$ and $Me_3N{\cdot}BF_3$. In the new species, Me_3N is apparently complexed with a new BF_2 acceptor site. ^1H N.m.r. spectra indicated two new species, apparently Me_3N adducts (major and minor absorptions at 2·84 and 2·75 p.p.m. respectively, in addition to the $n = 1$ adduct and $Me_3N{\cdot}BF_3$ peaks). ^{11}B N.m.r. spectra showed an unusual ratio of peaks due to free BF_2 (−34 p.p.m.), complexed BF_2 (−7 p.p.m.), and central boron (51 p.p.m.). The new species might be Me_3N adducts of higher homologues of (II). A study of the interactions of Me_3N with Si_2Cl_6 [9] provides precedent

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[7] H. Binder and E. Fluck, *Z. anorg. Chem.*, 1971, **381**, 116.

[8] R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, 1956, **78**, 1524.

[9] G. Urry, *J. Inorg. Nuclear Chem.*, 1964, **26**, 409.

for the formation of higher homologues of a Lewis acid in the presence of small amounts of Me_3N.

The Reaction of Me_3N *with* B_8F_{12}.—When excess of Me_3N was condensed on top of a frozen B_8F_{12} solution in methylene chloride at −196 °C and the mixture allowed to warm to −90 °C, a rapid reaction occurred. Boron trifluoride was evolved below the interface and then absorbed in the amine layer as $Me_3N{\cdot}BF_3$. After the −90 °C reaction was complete the solution gave a number of ^{19}F n.m.r. peaks in the 140—160 p.p.m. region, corresponding to fluorine on tetrahedral boron (*e.g.* at 146·0, 148·1, 151·5, and 156·8 p.p.m.), and a much larger resonance due to $Me_3N{\cdot}BF_3$ [164·3 p.p.m., $J(^{11}B-^{19}F)$ 15·1 Hz [5]]. There was also a peak at 78·0 p.p.m. but no peaks in the 40—55 p.p.m. region corresponding to the higher boron fluorides. Further warming to −20 °C had little effect on the spectrum.

When B_8F_{12} rather than Me_3N was present in excess, appreciable evolution of BF_3 occurred only on warming to −60 °C. Brief warming to −60 °C gave −90 °C ^{19}F n.m.r. peaks at 50·0 (B_8F_{12}), 121·7 (BF_3), 41·4, and 44·0 p.p.m. and a shoulder at 50·7 p.p.m. Warming to −20 °C for 1 min caused a large increase in the 44·0 p.p.m. peak and disappearance of the B_8F_{12} peak and most of the intensity of the 41·7 p.p.m. peak. Absence of $Me_3N{\cdot}BF_3$ or other fluorine-on-tetrahedral-boron peaks throughout this process indicates bonding of Me_3N to a strong Lewis-acid site not directly linked to fluorine. This is consistent with fission of B_8F_{12} to give $Me_3N{\cdot}B(BF_2)_3$. The single −90 °C ^1H n.m.r. peak (3·26 p.p.m., width at half height 8 Hz) corresponds to a large complexation shift [0·81 p.p.m. compared to $Me_3N{\cdot}BF_3$ (0·45 p.p.m.) and $F_3P{\cdot}B(BF_2NMe_3)(BF_2)_2$ (0·37 p.p.m.)], and this supports [5] interaction with a 'super-acid' site. Furthermore the BF_2 group of B_2F_4 is a weaker Lewis acid than BF_3 toward Me_3N; [10] since the BF_2 groups of B_8F_{12} are probably similar to those of B_2F_4, the absence of the BF_3 adduct when both BF_3 and B_8F_{12} are present in solution is indirect evidence of Me_3N association with the central boron of $B(BF_2)_3$. However, the meagre evidence allows only tentative identification of $Me_3N{\cdot}B(BF_2)_3$.

The initial adduct reacted extremely rapidly with any additional Me_3N present to give BF_3 and other products. From our work on the $Me_3N–F_3P{\cdot}B(BF_2)_3$ system it is clear that a second Me_3N should be able to complex with a BF_2 group of the initially formed adduct. The resulting species decomposes very rapidly since it lacks the special stability found in $F_3P{\cdot}B(BF_2)_3$ and maintained to some extent in $F_3P{\cdot}B(BF_2NMe_3)_n(BF_2)_{3-n}$ ($n = 1—3$). Since BF_3 gas is evolved, the complexed BF_2 group does not give rise to $Me_3N{\cdot}BF_3$ directly. A number of possibilities remain, but it will be difficult to carry out more detailed studies on this extremely reactive system.

A weak interaction of B_8F_{12} with dichloromethane is suggested by the 5·9 p.p.m. shift of the ^{19}F n.m.r. signal to high field in this solvent from its position in the pure liquid or in $CFCl_3$.[1] Survival of the chromophore in solution argues against any gross change in structure such as breaking apart of the dimer. It may be that the 'super-acid' B_8F_{12} is capable of interacting with the chlorine of dichloromethane; the halogen atoms of certain alkyl halides can apparently act as Lewis bases.[11] A much smaller solvation interaction is indicated for $F_3P{\cdot}B(BF_2)_3$ in dichloromethane (BF_2 resonance, 2·0 p.p.m. to high field; PF_3 resonance, 1·6 p.p.m. to low field).

In polyfunctional Lewis bases having nitrogen- and phosphorus-donor sites linked together, it has been shown that BF_3 prefers to combine with nitrogen whereas BH_3 prefers to combine with phosphorus.[12] In the $B(BF_2)_3$ moiety a similar situation exists, *i.e.* in this polyfunctional Lewis acid the different boron sites have their own strong preferences. Trifluorophosphine combines only with the central boron whereas NMe_3 can combine with any of the boron sites.

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[10] B. W. C. Ashcroft and A. K. Holliday, *J. Chem. Soc.* (*A*), 1971, 2581.

[11] M. Goldstein, L. I. B. Haines, and J. A. G. Hemmings, *J.C.S. Dalton*, 1972, 2260 and refs. therein.

[12] S. Fleming and R. W. Parry, *Inorg. Chem.*, 1972, **11**, 1; C. Jouany, J. P. Laurent, and G. Jugie, *J.C.S. Dalton*, 1974, 1510.