COMMUNICATION

ChemComm
www.rsc.org/chemcomm

# Unexpected formation of new fluoroboranes from the reaction of $NMe_4B_3H_8$ with $BF_3$ and MeC≡CH: *exo*-2-$FB_4H_9$ and *trans*-MeCH=$CHBF_2$†

**Mark A. Fox,[a] Robert Greatrex*[b] and Daniel L. Ormsby‡[b]**
[a] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*
[b] *Department of Chemistry, University of Leeds, Leeds, UK LS2 9JT. E-mail: r.greatrex@chem.leeds.ac.uk*

*Received (in Cambridge, UK) 24th June 2002, Accepted 22nd July 2002*
*First published as an Advance Article on the web 13th August 2002*

**The new fluoroboranes *exo*-2-$FB_4H_9$ 1 and *trans*-MeCH=$CHBF_2$ 2 have been obtained unexpectedly and in good yield from the reaction of tetramethylammonium octahydrotriborate ($NMe_4B_3H_8$) with boron trifluoride and propyne (MeC≡CH).**

Fluoropolyborane compounds such as fluorinated borane anions[1] and polyboron fluorides[2] are the subject of significant current interest. However, only one neutral polyborane containing a fluorine atom attached to a cluster boron atom has been reported, namely the pentaborane(9) derivative 2-$FB_5H_8$.[3] During the course of our investigations[4] into the role played by the reactive intermediate {$B_3H_7$} in the synthesis and mechanisms of formation of small carbaboranes we have now discovered, quite unexpectedly, a one-pot reaction that generates two new fluoroboranes, in good yield.

To avoid the difficulties involved in preparing and handling $B_3H_7CO$[5] we decided to continue this work by exploring the reaction of propyne with {$B_3H_7$} produced *in situ* by hydride-ion abstraction from $[B_3H_8]^-$. In the absence of alkyne the reaction of $NMe_4B_3H_8$ and $BF_3$ is known to generate pure $B_4H_{10}$ in high yield.[6] Surprisingly, in the presence of MeC≡CH at −20 °C for 3 h we now find that the main volatile products are 2-$FB_4H_9$ **1** and MeCH=$CHBF_2$ **2**.§ Tetraborane(10) is not observed. The new fluoroborane, *arachno*-2-$FB_4H_9$ **1**, is unstable above −20 °C, decomposing rapidly to $B_4H_{10}$ as the only volatile compound at room temperature, whereas **2** is stable at ambient temperature under nitrogen.

Boron–hydrogen couplings consistent with those expected for a tetraborane molecule with a substituent at the wingtip boron B2 were observed for boron atoms B1, B3 and B4 in the line-narrowed $^{11}B$ spectrum for 2-$FB_4H_9$ **1** (Fig. 1).¶ Couplings from bridging hydrogen atoms were obscured for B2 which couples to the terminal fluorine substituent. The proton-decoupled $^{11}B$ spectrum comprised three peaks with intensities in the ratio 1 : 1 : 2 and shifts of 10.5, −16.5 and −41.0 ppm, assigned to boron atoms B2, B4 and B1,3 respectively. However, as in other 2-substituted tetraboranes, such as 2-$BrB_4H_9$[7] and 2-$MeB_4H_9$,[8] the precise location (*exo* or *endo*) of the fluorine substituent in **1** could not be established from the NMR spectroscopic data alone.

Optimised geometries of 2-$FB_4H_9$ **1** at the correlated MP2/6-31G* level of theory showed the *exo* isomer **1a** to be more stable than the *endo* isomer **1b** by 2.2 kcal $mol^{-1}$ (Fig. 2).‖ Moreover, as indicated in Table 1, comparison of calculated (GIAO-B3LYP/6-311G*) chemical shifts generated from these optimised geometries with the shifts observed experimentally confirms that the fluorotetraborane is indeed the *exo*-isomer **1a**. *Ab initio* calculations (see ESI†) on the related boranes 2-$MeB_4H_9$ and 2-$BrB_4H_9$ indicate that the *exo* configuration is the more stable in each case.

*trans*-MeCH=$CHBF_2$ **2**, a derivative of $CH_2$=$CHBF_2$,[9] was characterised by multinuclear ($^1H$, $^{11}B$, $^{19}F$ and $^{13}C$) NMR spectroscopy and mass spectrometry. The *trans*-configuration in **2** was indicated by the coupling constant of 18 Hz for $^3J$HC=CH, which falls within the range expected for *trans*-RCH=CHR′ isomers.[10] Further evidence in favour of the *trans*

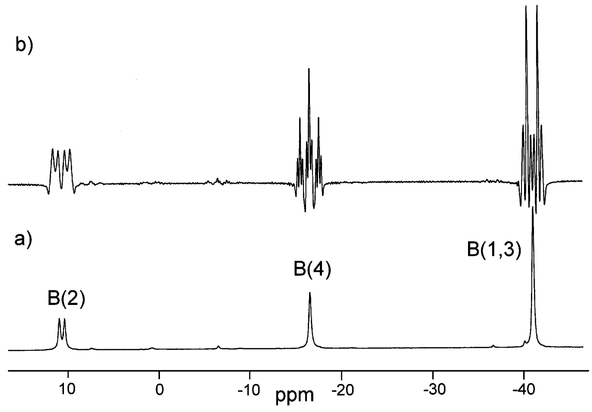
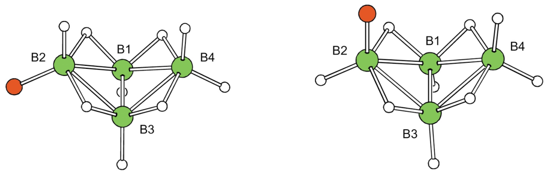
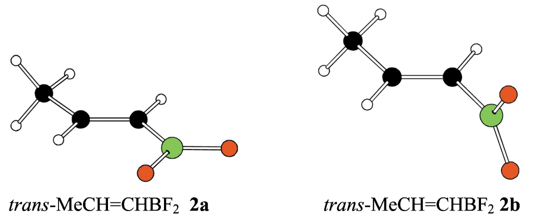


**Fig. 1** Boron NMR spectra for 2-$FB_4H_9$ **1**; (a) proton-decoupled and (b) line-narrowed.



*exo*-2-$FB_4H_9$ **1a** *endo*-2-$FB_4H_9$ **1b**



*trans*-MeCH=$CHBF_2$ **2a** *trans*-MeCH=$CHBF_2$ **2b**

**Fig. 2** Optimised geometries of 2-$FB_4H_9$ **1** and *trans*-MeCH=$CHBF_2$ **2**.

**Table 1** Observed (**1**) and calculated (**1a** and **1b**) $^{11}B$, $^1H$ and $^{19}F$ NMR chemical shifts for 2-$FB_4H_9$

| | **1a** | **1** | **1b** |
|---|---|---|---|
| B2 | 8.1 | 10.5 | 18.5 |
| B4 | −19.5 | −16.8 | −11.0 |
| B1,3 | −47.7 | −42.2 | −42.6 |
| H2 | 4.07 | 3.64 | 4.90 |
| *endo*-H4 | 2.35 | 1.92 | 3.81 |
| *exo*-H4 | 2.32 | 1.92 | 2.73 |
| *exo*-H1,3 | 1.75 | 1.40 | 1.75 |
| μ-H1/2,2/3 | 0.79 | 0.95 | 1.07 |
| μ-H1/4,3/4 | −1.76 | −1.32 | −1.14 |
| F | −142 | −152 | −170 |

DOI: 10.1039/b206102c

---

† Electronic supplementary information (ESI) available: boron NMR shifts and relative energies for 2-$MeB_4H_9$ and 2-$BrB_4H_9$ and .xyz files. See http://www.rsc.org/suppdata/cc/b2/b206102c/

‡ Current address: Accelrys Ltd., 334 Cambridge Science Park, Cambridge, UK CB4, 0WN.

configuration was provided by the excellent agreement between the experimental NMR chemical shifts with those calculated from the *ab-initio* optimised geometry **2a** in which the fluorine atoms lie in the same plane as the double bond (Fig. 2). The barrier to rotation of the $BF_2$ group about the B–C bond vector *via* **2b** was computed to be 6.8 kcal $mol^{-1}$, very similar to the value of 4.56 kcal $mol^{-1}$ determined recently by variable temperature $^{19}F$ NMR spectroscopy for the related vinyldifluoroborane.[11] Examination of the orbitals computed for the optimised geometries **2a** and **2b** revealed a small interaction in the HOMO for **2a** between the C=C π-orbital and the vacant boron π-orbital which is absent in the HOMO for **2b**. This interaction in **2a**, which may be described as hyperconjugation, is largely responsible for the rotational barrier.

The overall stoichiometry, as indicated in the following oversimplified scheme, indicates that three moles of $BF_3$ are required for one mole of **1** and one of **2**, and on this basis the yield for **2** is 69%.

$$[B_3H_8]^- + BF_3 \rightarrow \{B_3H_7\} + [HBF_3]^-$$

$$2\{B_3H_7\} + BF_3 + MeC{\equiv}CH \rightarrow B_4H_9F\ (\mathbf{1}) + MeCH{=}CHBF_2\ (\mathbf{2}) + {}^1/_n(B_2H_4)_n$$

$$2[B_3H_8]^- + 3BF_3 + MeC{\equiv}CH \rightarrow B_4H_9F\ (\mathbf{1}) + 2[HBF_3]^- + MeCH{=}CHBF_2\ (\mathbf{2}) + {}^1/_n(B_2H_4)_n$$

In considering the mechanism of this reaction, several additional pieces of experimental evidence are highly informative: (i) no reaction occurs at 0 °C between $B_4H_{10}$ and $BF_3$ in the presence of propyne, (ii) no reaction takes place when 6 mmol each of $B_4H_{10}$ and MeC≡CH are condensed into a flask containing the solid ‘$[HBF_3]^-$’, and stirred for 4 h at 0 °C, (iii) no reaction is observed between $BF_3$ and propyne in the absence of $[B_3H_8]^-$.

From these observations it is clear that the fluorotetraborane does not result from the rapid reaction with either $BF_3$ or $[HBF_3]^-$ of any $B_4H_{10}$ that might have been formed *in situ*. It therefore seems reasonable to conclude that the first step does indeed involve the abstraction of a hydride ion from $[B_3H_8]^-$ to generate $\{B_3H_7\}$, but that this reactive intermediate (which in the absence of propyne would react with itself to give $B_4H_{10}$) is then trapped by the alkyne in a hydroboration process. The resulting intermediate (presumably $MeCH{=}CHB_3H_6$), could then react with $BF_3$ in a double displacement reaction to yield the fluoroborane **2** and $\{B_3H_6F\}$. Subsequent reaction of the latter with $\{B_3H_7\}$ would account for the formation of the fluorotetraborane **1**. This interpretation of the evidence implies that, under the conditions of the experiment, $\{B_3H_7\}$ reacts more readily with both the alkyne and $\{B_3H_6F\}$ than with itself.

In summary, the syntheses of *exo*-2-$FB_4H_9$ **1** and *trans*-$MeCH{=}CHBF_2$ **2** have been obtained unexpectedly, in good yields, from a one-pot reaction involving commercially available starting materials. The known compounds, 2-bromotetraborane[6,7] and vinyldifluoroborane,[9] related respectively to **1** and **2**, have been reported as products from difficult, multi-step syntheses, the latter involving divinylmercury as a reagent. The present study suggests that these compounds might be obtained much more conveniently from the appropriate boron trihalide and alkyne. There is also scope for extending this work to the exploration of reactions involving other borane anions and unsaturated hydrocarbons.

We thank the EPSRC for funding, for the award of an EPSRC Advanced Research Fellowship to M. A. F., and a quota award to D. L. O.

## Notes and references

§ *Syntheses, separation and mass spectra of* $B_4H_9F$ **1** and $MeCH{=}CHBF_2$ **2**: the gases $BF_3$ (13 mmol) and MeC≡CH (13 mmol) were condensed at −196 °C into a 1 l flask containing 3.03 g (13 mmol) of $NMe_4B_3H_8$ and a magnetic stirrer bar. The flask was warmed to −20 °C (carbon tetrachloride–liquid nitrogen slush) for 3 h followed by cooling to −196 °C and the non-condensable gas (probably $H_2$) was removed by evacuation. The volatile products were then subjected to cold-column fractionation,[12] with mass spectrometric monitoring. The products were collected in order of decreasing volatility (highest mass cut-off and % yield based on the total volatile product fraction in parentheses) $B_2H_6$ (*m/z* 28, 5%), *trans*-$MeCH{=}CHBF_2$ **2** (*m/z* 90, 40%), 2-$FB_4H_9$ **1** (*m/z* 38, 30%) and $B_5H_9$ (*m/z* 64, 10%). The parent mass cut-off for the fluoroborane **1** is not observed and the mass cut-off of 38 is likely to be $F_2$. The yield of the stable compound *trans*-$MeCH{=}CHBF_2$ **2** was *ca* 3 mmol.

¶ NMR data for **1** (in $CDCl_3$ at 233 K): $\delta_B$ 10.5 (dd, $J$BHt = 174 Hz, $J$BF 75; B2), −16.8 (tt, $J$BHt 132, $J$BHμ 38; B4), −42.2 (dt, $J$BHt 150, $J$BHμ 54; B1, B3). $^1H$ NMR: $\delta_H$ 3.64 (d, $^2J$HBF 38; B2H), 1.92 (s; B4H), 1.40 (s; B1H, B3H), 0.95 (s; Hμ1/2, Hμ2/3), −1.32 (s; Hμ3/4, Hμ1/4), $\delta_F$ −152 (br). NMR data for **2**: $\delta_B$ 24.1 (t, $J$BF = 66 Hz). $^1H$ NMR: $\delta_H$ 7.02 (dq, $^3J$HC=CH 18, $^3J$HCCH$_3$ 6.5; CHCH$_3$), 5.41 (dtq, $^3J$HC=CH 18, $^3J$HCBF$_2$ 6, $^4J$HC=CHCH$_3$ 1; CHBF$_2$), 1.95 (d, $^3J$HCCH$_3$ 6.5; CH$_3$), $\delta_C$ 159.2 (t, $^4J$C=CBF 18; CH$_3$CH), 117.7 (s br; CHBF$_2$), 22.4 (s; CH$_3$), $\delta_F$ −89 (br).

‖ *Computational*: all *ab initio* computations were carried out with the Gaussian 94 package.[13] The geometries **1a**, **1b**, **2a** and **2b** were initially optimised at the HF/6-31G* level. Frequency calculations were computed on these optimised geometries at the HF/6-31G* level for imaginary frequencies. Optimisations of these geometries were then carried out at the computationally intensive MP2/6-31G* level. NMR shifts were calculated on these MP2/6-31G* geometries at the GIAO-B3LYP/6-311G* level. Theoretical $^{11}B$ chemical shifts listed in the table and in the experimental section have been referenced to $B_2H_6$ (16.6 ppm) and converted to the usual $BF_3{\cdot}OEt_2$ scale; $\delta(^{11}B) = 102.83 - \sigma(^{11}B)$. $^{13}C$ and $^1H$ chemical shifts were referenced to TMS; $\delta(^{13}C) = 184.11 - \sigma(^{13}C)$, $\delta(^1H) = 32.28 - \sigma(^1H)$. $^{19}F$ chemical shifts were referenced to HF and converted to the usual $CFCl_3$ scale; $\delta(^{19}F) = 185 - \sigma(^{19}F)$. Calculated NMR data from geometry **2a** $\delta_B$ 24.3, $\delta_H$ 7.39 (CHCH$_3$), 5.42 (CHBF$_2$), 1.97 (CH$_3$), $\delta_C$ 169.6 (CH$_3$CH), 124.0 (CHBF$_2$), 25.3 (s; CH$_3$), $\delta_F$ −74.

Cartesian coordinates and relative energies of optimised geometries of 2-$FB_4H_9$ (**1a**, **1b**), *trans*-$MeCH{=}CHBF_2$ (**2a**, **2b**), 2-$MeB_4H_9$ and 2-$BrB_4H_9$ and calculated NMR shifts generated from optimised geometries of 2-$MeB_4H_9$ and 2-$BrB_4H_9$ are available as ESI†.

1 H. Thomsen, O. Haeckel, U. Krause and W. Preetz, *Z. Anorg. Allg. Chem.*, 1996, **622**, 2061; S. H. Strauss, *Special Publication of the Royal Society of Chemistry*, RSC, Cambridge, UK, 2000, vol. 253, pp. 46–48 and references therein.

2 P. T. Brain, D. W. H. Rankin, H. E. Robertson, I. L. Alberts, M. Hofmann and P. v. R. Schleyer, *Inorg. Chem.*, 1994, **33**, 2565; J. C. Jeffery, N. C. Norman, J. A. J. Pardoe and P. L. Timms, *Chem. Commun.*, 2000, 2367; J. A. J. Pardoe, N. C. Norman and P. L. Timms, *Polyhedron*, 2002, **21**, 543.

3 A. B. Burg, *J. Amer. Chem. Soc.*, 1968, **90**, 1407.

4 M. A. Fox, R. Greatrex, N. N. Greenwood and M. Kirk, *Coll. Czech. Chem. Commun.*, 1999, **64**, 806.

5 R. T. Paine and R. W. Parry, *Inorg. Chem.*, 1969, **8**, 2461; J. D. Glore, J. W. Rathke and R. Schaeffer, *Inorg. Chem.*, 1973, **12**, 2175.

6 M. A. Toft, J. B. Leach, F. L. Himpsl and S. G. Shore, *Inorg. Chem.*, 1982, **21**, 1952.

7 J. Dobson and R. Schaeffer, *Inorg. Chem.*, 1965, **4**, 593.

8 W. R. Deever and D. M. Ritter, *Inorg. Chem.*, 1969, **8**, 2461.

9 F. E. Brinckman and F. G. A. Stone, *J. Chem. Soc.*, 1960, **82**, 6218; T. D. Coyle and F. G. A. Stone, *J. Chem. Soc.*, 1960, **82**, 6223; T. D. Coyle, S. L. Stafford and F. G. A. Stone, *J. Chem. Soc.*, 1961, 3103; A. K. Holliday and F. B. Taylor, *J. Chem. Soc.*, 1964, 2731; J. R. Durig, R. O. Carter and J. D. Odom, *Inorg. Chem.*, 1974, **13**, 701; T. Onak, M. Diaz and M. Barfield, *J. Am. Chem. Soc.*, 1995, **117**, 1403.

10 R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th edn., J. Wiley and Sons, New York, 1981, 235.

11 D. M. Pawar, R. Parks, M. Price, D. Reese and E. A. Noe, *J. Mol. Struct.*, 2000, **525**, 209.

12 J. Dobson and R. Schaeffer, *Inorg. Chem.*, 1970, **9**, 2183; D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-sensitive Compounds*, 2nd edn. Wiley-Interscience, New York (1986), p.193.

13 Gaussian 94, Revision E.2, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, USA, 1995.