Journal of Organometallic Chemistry, 294 (1985) 23–30
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CRYSTAL AND MOLECULAR STRUCTURE OF FLUORO(HYDROXY){TRIS(DIMETHYLPHENYLSILYL)METHYL}BORANE

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(Received April 19th, 1985)

Summary

The compound $(Me_2PhSi)_3CBF(OH)$, made by the hydrolysis of $(Me_2PhSi)_3CBF_2$, appears to be the first fully characterised organofluorohydroxyborane. The coordination at boron is almost planar. Steric interactions from the large alkyl group, which adopts a propeller-like conformation, compress the F–B–O angle to 111(1)°, prevent intermolecular hydrogen bonds, and largely determine the crystal packing. As a result, the orientation of the FBO plane with respect to the three C–Si bonds is disordered: in one orientation (occupancy 40%) the FBO plane eclipses one of the C–Si bonds and in the other (occupancy 60%) the FBO plane is turned through approximately 90°.

Introduction

Alkylboronic acids $RB(OH)_2$ and alkyldifluoroboranes RBF_2 are well known, but, as far as we are aware, no organofluorohydroxyborane RBF(OH) has been characterised. We recently isolated difluoro{tris(dimethylphenylsilyl)methyl}borane [1] and noticed that it was easily hydrolysed by atmospheric moisture to the compound TpsiBF(OH) (Tpsi = $(Me_2PhSi)_3C$). In order to confirm the spectroscopic evidence for the new class of compound and to explore whether molecules are linked by intermolecular hydrogen bonds similar to those in the isoelectronic carboxylic acids RCO(OH), we isolated crystals which proved to be suitable for a structural determination.

Experimental

A mixture of $TpsiBF_2$ [1] (0.50 g, 1 mmol), water (3 ml) and THF (10 ml) was stirred at 20°C for 3 h. The product was extracted into petroleum ether (b.p.

0022-328X/85/$03.30

30–40°C) and the extract was dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue, which was sublimed at 175°C/0.01 Torr and subsequently recrystallised from heptane, was TpsiBF(OH) (0.45 g, 90%), m.p. 183–185°C (Found: C, 63.7; H, 7.7. $C_{25}H_{34}BFOSi_3$ calcd.: C, 64.6; H, 7.3%). δ(H) (CCl_4 vs. TMS): 0.24 (18H, s, SiMe), 4.85 (1H, d, ^{2}J(FH) 10.3 Hz, reduced on addition of D_2O, OH) 7.2–7.6 (15H, m, Ph); δ(F) ($CDCl_3$ vs. $CFCl_3$) −63.3 δ(B) ($CDCl_3$ vs. BF_3OEt_2) 29.3. Both the ^{19}F and the ^{11}B peaks were too broad to show spin–spin coupling. The IR spectrum showed a sharp absorption at 3640 cm^{-1}, and the mass spectrum peaks at m/z (intensities relative to the base peak at m/z 135 $[Me_2PhSi]^+$ in parentheses) 464 (1%, M^+), 449 (5 $[M-Me]^+$), 444 (2, $[M-HF]^+$), 429 (30, $[M-Me-HF]^+$), 371 (50, $[M-Me-C_6H_6]^+$), 309 (30, $[(Me_2PhSi)_2CBO]^+$).

Crystal data

$C_{25}H_{34}BFOSi_3$ $M = 464.7$, Monoclinic, a 8.721(9), b 19.508(4), c 15.490(3) Å, β 93.06(5)°, V 2631 Å^3 (by least-squares refinement of 24 centered reflections, λ 0.71069 Å). Space group $P2_1/a$, $Z = 4$, D_c 1.18 g cm^{-3}. Crystal dimensions 0.4 × 0.4 × 0.5 mm, μ (Mo-K_α) 1.97 cm^{-1}.

Data collection and processing

Data were collected as described previously [2] on an Enraf–Nonius CAD4 diffractometer using a $\theta/2\theta$ scan with scan width 0.8 + 0.2tanθ. From 3719 reflections having $1 < \theta < 44°$, 1674 with $I > 2\sigma(I)$ were used in the structure determina-

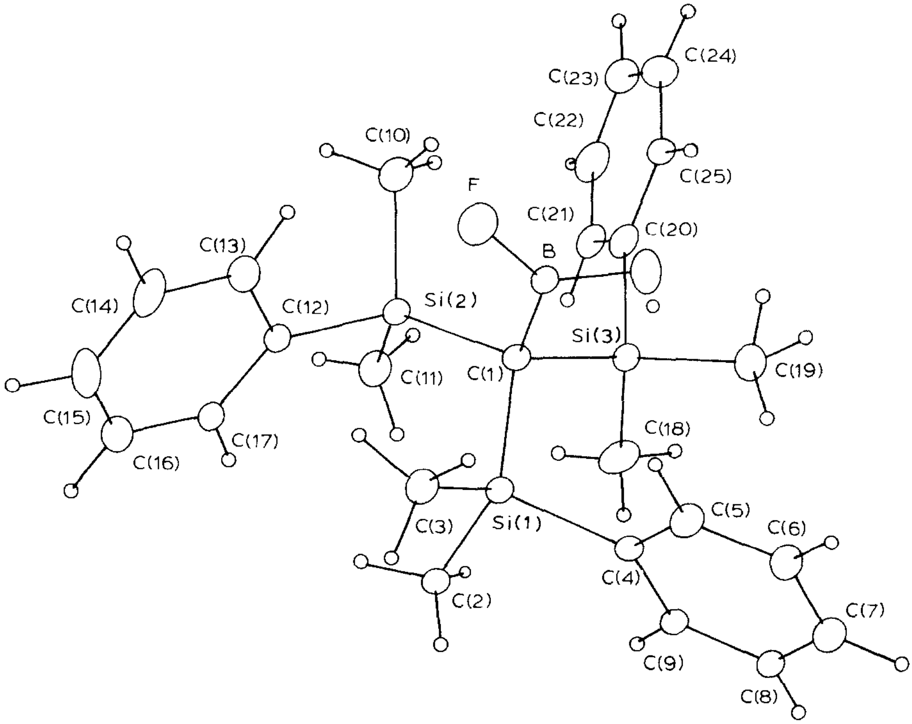

Fig. 1. The structure of $(Me_2PhSi)_3CBF(OH)$.

tion. Three standard reflections showed less than 5% decay during collection of data, which were corrected for Lorentz and polarisation effects but not for absorption or extinction.

Structure analysis and refinement

The direct methods program MULTAN [3] gave the positions of the CSi_3 group, and the remaining non-hydrogen atoms were found on a difference Fourier map generated by the SHELX [4] system. At this point disorder was noted in the positions of the oxygen and fluorine atoms. Separate refinement of the positional and thermal parameters and of the occupancy factors (constrained to total 1.0) showed that the FBO plane had two orientations: one with occupancy 0.6 and the other, denoted F(1)BO(1), with occupancy 0.4. After refinement of non-hydrogen atoms with anisotropic thermal parameters, a low angle difference map revealed the

TABLE 1

FRACTIONAL ATOMIC COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Si(1)	0.4025(2)	0.13308(9)	0.2679(1)
Si(2)	0.1792(2)	0.03028(9)	0.3599(1)
Si(3)	0.3040(2)	−0.00727(9)	0.1764(1)
C(1)	0.2442(6)	0.0646(3)	0.2518(3)
C(2)	0.5616(6)	0.1063(4)	0.3457(4)
C(3)	0.3266(8)	0.2160(3)	0.3068(5)
C(4)	0.4922(6)	0.1539(3)	0.1623(4)
C(5)	0.4188(7)	0.1964(3)	0.1008(4)
C(6)	0.4819(8)	0.2106(3)	0.0229(4)
C(7)	0.6203(8)	0.1828(4)	0.0044(5)
C(8)	0.6975(7)	0.1421(4)	0.0635(4)
C(9)	0.6356(6)	0.1276(3)	0.1423(4)
C(10)	−0.0141(6)	−0.0108(3)	0.3496(4)
C(11)	0.3122(7)	−0.0352(3)	0.4091(4)
C(12)	0.1646(7)	0.1000(3)	0.4433(4)
C(13)	0.0354(7)	0.1426(3)	0.4437(4)
C(14)	0.021(1)	0.1927(4)	0.5063(6)
C(15)	0.132(1)	0.2001(4)	0.5710(5)
C(16)	0.2578(9)	0.1587(4)	0.5737(4)
C(17)	0.2730(7)	0.1095(3)	0.5111(4)
C(18)	0.4967(6)	−0.0439(3)	0.2056(5)
C(19)	0.3091(8)	0.0202(3)	0.0628(4)
C(20)	0.1626(7)	−0.0814(3)	0.1768(4)
C(21)	0.1939(8)	−0.1417(4)	0.2216(4)
C(22)	0.088(1)	−0.1945(4)	0.2208(5)
C(23)	−0.051(1)	−0.1878(5)	0.1770(6)
C(24)	−0.0819(9)	−0.1303(5)	0.1297(5)
C(25)	0.0212(8)	−0.0769(4)	0.1295(4)
B	0.1042(7)	0.1010(4)	0.2060(4)
F	−0.0054(8)	0.1315(5)	0.2442(5)
O	0.093(1)	0.1124(6)	0.1175(5)
O(1)	−0.027(1)	0.0661(5)	0.1817(8)
F(1)	0.095(1)	0.1630(5)	0.1832(8)

positions of all but the hydroxyl hydrogen atoms. Further refinement with these riding on the relevant carbon atoms converged at $R = 0.043$ and $R' = 0.043$. Unit weights were used throughout and no feature > 0.1 e A^{-3} was observed on the final

TABLE 2

PRINCIPAL INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

B–F	1.29(1)	B–F(1)	1.26(1)
B–O	1.38(1)	B–O(1)	1.37(1)
B–C(1)	1.549(8)	Si(1)–C(1)	1.925(5)
Si(1)–C(2)	1.857(6)	Si(1)–C(3)	1.857(7)
Si(1)–C(4)	1.890(6)	Si(2)–C(1)	1.912(5)
Si(2)–C(10)	1.863(6)	Si(2)–C(11)	1.859(6)
Si(2)–C(12)	1.880(6)	Si(3)–C(1)	1.911(5)
Si(3)–C(18)	1.857(6)	Si(3)–C(19)	1.837(6)
Si(3)–C(20)	1.897(6)	C(4)–C(5)	1.389(8)
C(4)–C(9)	1.400(8)	C(5)–C(6)	1.377(9)
C(6)–C(7)	1.37(1)	C(7)–C(8)	1.36(1)
C(8)–C(9)	1.386(9)	C(12)–C(13)	1.399(9)
C(12)–C(17)	1.385(8)	C(13)–C(14)	1.38(1)
C(14)–C(15)	1.36(1)	C(15)–C(16)	1.36(1)
C(16)–C(17)	1.37(1)	C(20)–C(21)	1.384(9)
C(20)–C(25)	1.400(9)	C(21)–C(22)	1.38(1)
C(22)–C(23)	1.36(1)	C(23)–C(24)	1.36(1)
C(24)–C(25)	1.37(1)		
Mean C–H(Me)	0.99(1)	Mean C–H(Ph)	1.00(1)
F–B–O	111.3(7)	F(1)–B–O(1)	110.8(7)
F–B–C(1)	125.7(6)	F(1)–B–C(1)	127.3(6)
O–B–C(1)	122.5(7)	O(1)–B–C(1)	121.8(7)
C(1)–Si(1)–C(2)	113.4(3)	C(1)–Si(1)–C(3)	112.3(3)
C(2)–Si(1)–C(3)	107.2(3)	C(1)–Si(1)–C(4)	111.3(2)
C(2)–Si(1)–C(4)	106.9(3)	C(3)–Si(1)–C(4)	105.3(3)
C(1)–Si(2)–C(10)	112.6(3)	C(1)–Si(2)–C(11)	113.0(3)
C(10)–Si(2)–C(11)	106.3(9)	C(1)–Si(2)–C(12)	112.3(2)
C(10)–Si(2)–C(12)	106.0(3)	C(11)–Si(2)–C(12)	106.1(3)
C(1)–Si(3)–C(18)	113.9(3)	C(1)–Si(3)–C(19)	113.0(3)
C(18)–Si(3)–C(19)	106.1(3)	C(1)–Si(3)–C(20)	111.0(3)
C(18)–Si(3)–C(20)	106.6(3)	C(19)–Si(3)–C(20)	105.8(3)
B–C(1)–Si(1)	106.4(4)	Si(1)–C(1)–Si(2)	111.9(2)
B–C(1)–Si(2)	107.3(4)	Si(1)–C(1)–Si(3)	111.7(3)
Si(2)–C(1)–Si(3)	112.3(3)	B–C(1)–Si(3)	106.8(4)
Si(1)–C(4)–C(5)	121.5(4)	Si(1)–C(4)–C(9)	121.7(4)
C(5)–C(4)–C(9)	116.8(5)	C(4)–C(5)–C(6)	121.8(6)
C(5)–C(6)–C(7)	120.0(6)	C(6)–C(7)–C(8)	120.1(7)
C(7)–C(8)–C(9)	120.5(8)	C(4)–C(9)–C(8)	120.8(5)
Si(2)–C(12)–C(13)	121.0(4)	Si(2)–C(12)–C(17)	123.2(5)
C(13)–C(12)–C(17)	115.6(5)	C(12)–C(13)–C(14)	121.5(6)
C(13)–C(14)–C(15)	120.3(8)	C(14)–C(15)–C(16)	119.9(8)
C(15)–C(16)–C(17)	120.0(7)	C(12)–C(17)–C(16)	122.7(6)
Si(3)–C(20)–C(21)	122.5(5)	Si(3)–C(20)–C(25)	120.3(5)
C(21)–C(20)–C(25)	117.2(8)	C(20)–C(21)–C(22)	121.0(7)
C(21)–C(22)–C(23)	120.5(8)	C(22)–C(23)–C(24)	119.5(9)
C(23)–C(24)–C(25)	121.0(8)	C(20)–C(25)–C(24)	120.6(7)

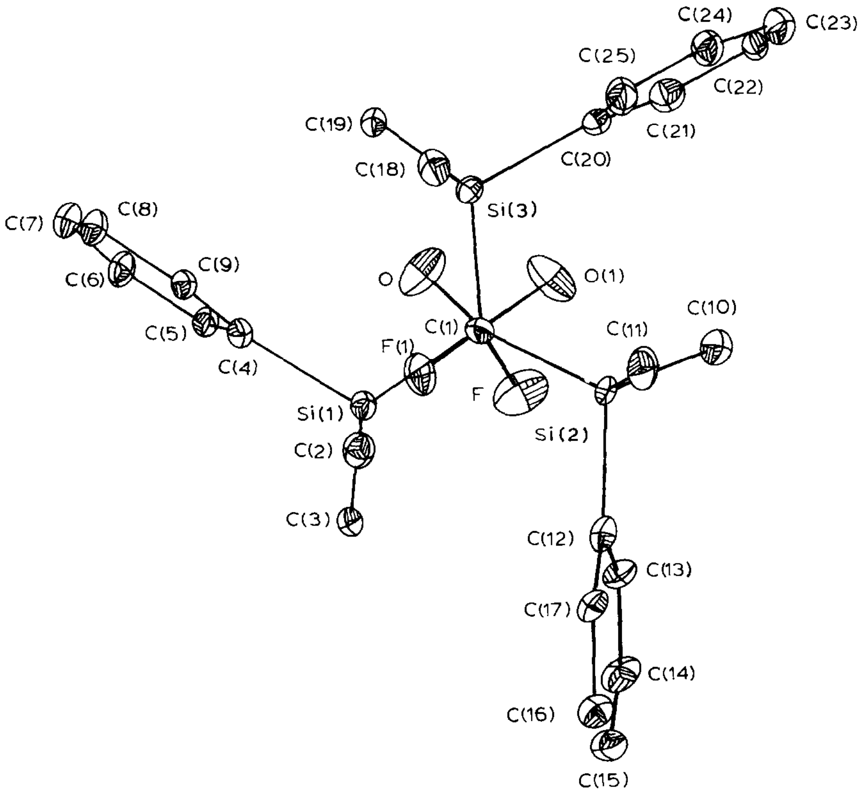

Fig. 2. The structure of $(Me_2PhSi)_3CBF(OH)$ viewed along the B–C(1) bond showing the two orientations of the BFO plane.

difference map. Scattering factors for non-hydrogen atoms were taken from ref. 5 and those for hydrogen from ref. 6.

Final fractional atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. A view of the molecule is shown in Fig. 1 and a view down the B–C bond in Fig. 2. Lists of structure factors, temperature factors and hydrogen atom coordinates are available from the authors.

Discussion

The structural determination confirms that an organofluorohydroxyborane TpsiBF(OH) has been isolated. We think that this is the first compound having an organic group, halogen, and hydroxide attached to boron to be characterised in the solid state. The compounds BF_2OH [7], $BF(OH)_2$, and HBF(OH) [8] have been identified as species in gaseous mixtures by microwave or mass [9] spectroscopy, and the ion $[BF_3OH]^-$ has been detected by potentiometric methods and by ^{19}F NMR [10] and IR spectroscopy [11]. Attempts to characterise $[BF_3OH^-]$ by X-ray methods [12–14] were not entirely satisfactory because the data were not sufficiently precise to distinguish unequivocally between OH and F.

The most interesting feature of the structure of TpsiBF(OH) is that the molecules

TABLE 3

MOLECULAR PARAMETERS IN TRIS(DIMETHYLPHENYLSILYL)METHYL COMPOUNDS

	$(PhMe_2Si)_3CH$	$(PhMe_2Si)_3CLi(THF)$	$(PhMe_2Si)_3CBH_3^-$	$(PhMe_2Si)_3CBF(OH)$
C–Si (Å)	1.895(1)	1.85(7)	1.88(2)	1.916(5)
Si–Me (Å)	1.850(2)	1.85(3)	1.90(2)	1.855(6)
Si–Ph (Å)	1.887(2)	1.90(3)	1.91(2)	1.889(6)
Me–Si–Me (°)	108.8(1)	101(2)	105.8(9)	106.5(3)
C–Si–Ph (°)	111.2(1)	111(4)	113.2(8)	111.5(3)
C–Si–Me (°)	112.4(5)	117(4)	113.5(9)	113.0(3)
Ph–Si–Me (°)	105.7(15)	105(1)	105.0(8)	106.1(3)
Si–C–Si (°)	114.0(1)	118(2)	113(1)	112.0(4)
Ph vs. Si_3 (°) [a]	85		75, 76, 85	80.8, 80.5, 80.8
Ref.	15	16,17	1, 16	This work

[a] Angles between plane of phenyl group and Si_3 plane.

in the crystal are discrete, with no intermolecular hydrogen bonds. The propeller-like configuration of the Tpsi group is very similar to that in TpsiH [15] or $TpsiBH_3Li(THF)_3$ [1,16]; in all cases (Table 3) the symmetry is almost (precisely in TpsiH) C_3, with the phenyl groups inclined at about 80° to the Si_3 plane. Distortion is significant only in TpsiLi(THF) [17], where there is intramolecular interaction between the lithium and one of the three phenyl groups. Within the Tpsi group the Si–C–Si angles are larger and the C–Si–C angles are smaller than the tetrahedral values, and within the phenyl groups the CCC angles (Table 2) adjacent to the silicon are slightly but significantly less than 120°, as found in many organometallic compounds having Ph–metal bonds [18]. The large alkyl groups dominate the crystal packing: the well-ordered array allows the positions of all the hydrogen atoms of the methyl and phenyl groups attached to silicon to be found.

The FBO fragment of the molecule is, however, disordered in a surprising way. In 60% of the molecules, the FBO plane is perpendicular to one of the three possible BC(1)Si planes (Fig. 2), with the fluorine on the same side as the two methyl groups attached to silicon. There are two further equivalent orientations of the FBO plane inclined at ±60°, but these are not adopted: instead the remaining molecules have FBO planes rotated through 90°, i.e. in an orientation which eclipses the original BC(1)Si plane. For each of the two orientations the coordination at boron is almost planar.

The mean B–F distance (1.28(1) Å) is apparently shorter than that in BF_3 (1.309(1) Å) and in other RBF_2 compounds (cf. $MeBF_2$ [20] 1.315(5), $PhBF_2$ [21] 1.330, F_2BOH [7] 1.32(2) Å), but in view of the large estimated standard deviation it is not clear whether the difference is significant; B–F bonds are usually shorter than is predicted for a single bond (1.37 Å) [20]. The B–C distance (1.549(8) Å) and the mean B–O distance (1.38(1) Å) are normal (cf. B–C: $MeBF_2$ [20] 1.564(5), $PhBF_2$ [21] 1.551, $PhB(OH)_2$ [22] 1.560(3) Å. B–O: $PhB(OH)_2$ 1.361(3), F_2BOH 1.34(2), Me_2BOMe 1.361(2), $MeB(OMe)_2$ 1.375(4) Å) [23]). The mean FBO angle (111.0(8)°) is, however, much less than 120°. Although factors determining bond angles at boron are not well understood [20] (cf. FBF in $MeBF_2$ 116.8(5)°, OBO in $PhB(OH)_2$ 116.3(2)°, but FBO in BF_2OH 122.8(10)°) there seems little doubt that in TpsiBF(OH) the FBO angle is compressed by steric hindrance from the large alkyl group. The data for TpsiBF(OH) are sufficiently precise to distinguish between F and OH: a random distribution between the two possible positions adjacent to each boron, which could not be ruled out in earlier X-ray determinations on similar compounds [12–14], is not found in this case. The configurations shown in Fig. 2 (and their mirror images) are thus experimentally observed: the configurations with oxygen and fluorine interchanged are not.

The shortest O ··· F contact is > 6 Å, so there is no intermolecular hydrogen bonding between BF(OH) groups similar to that between CO(OH) groups of carboxylic acids in the solid or in solution [24], between $B(OH)_2$ groups in $PhB(OH)_2$ [22], or within the hydrogen bonded tetramers of solid $Bu^t{}_2SiF(OH)$ [25]. The intramolecular distances O ··· F (2.135 Å) or O(1) ··· F(1) (2.233 Å) are close to the sum of the one angle radii (2.21 Å) [26]. It seems unlikely that the hydroxyl hydrogen atom is anchored by hydrogen bonding to the fluorine atom in the same molecule since it would probably then have been located in the structure determination. The absence of hydrogen bonding is also indicated by the sharp O–H stretching absorption in the IR. There are many intermolecular C ··· C contacts which are < 4 Å; these involve both methyl and phenyl groups, and reflect the way in which the bulky alkyl groups determine the crystal packing. There are also several F ··· Me and F ··· Ph contacts < 4 Å which are probably crucial in determining the two positions of low potential energy for the orientation of the FBO coordination plane with respect to the C_3 axis of the alkyl group.

It is likely that the compounds RBF(OH) normally decompose to boroxines $(RBO)_3$ and HF by an intermolecular process involving nucleophilic attack of oxygen of one molecule on the boron of another with subsequent loss of HF. This is probably greatly inhibited by the bulky Tpsi group, making possible the isolation of the fluoro(hydroxy) derivative.

Acknowledgements

We thank the NSF for financial support (to JLA and SGB), the SERC for financial support (to CE), the Libyan Government for a scholarship (to MNA El-K), and Dr. P.B. Hitchcock for helpful discussions.

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