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Note

Synthesis and Structure of the Dimethyl Sulfide Adducts of Mono- and Bis(pentafluorophenyl)borane

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*Summary: The borane dimethyl sulfide adduct $H_3B \cdot SMe_2$ and the diethyl ether adduct of tris(pentafluorophenyl)borane, $(C_6F_5)_3B \cdot OEt_2$, undergo facile exchange of hydride and pentafluorophenyl ligands, yielding $(C_6F_5)_2HB \cdot SMe_2$ (**1**) and $(C_6F_5)H_2B \cdot SMe_2$ (**2**) depending upon the ratio of reagents used. In the presence of excess dimethyl sulfide, both compounds can be isolated as colorless crystals, which have been structurally characterized.*

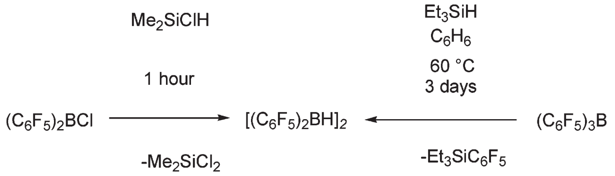
Introduction

Bis(pentafluorophenyl)borane [Piers' reagent, $(C_6F_5)_2HB$] was first reported in 1995.[1,2] In the solid state the structure is dimeric, but significant dissociation to the monomeric species occurs in solution. Piers' reagent is highly effective and regioselective for the hydroboration reactions of alkenes, alkynes,[3] vinyl silanes,[4] or allyl phosphines.[5]

The original preparation of $[(C_6F_5)_2HB]$ employed synthetically demanding $(C_6F_5)_2ClB$ as the immediate precursor, which is then converted to the borane using Me_2SiHCl (Scheme 1).[1] An alternative synthetic method starting with commercially available $(C_6F_5)_3B$ and Et_3SiH was reported shortly afterward.[2]

Like $(C_6F_5)_3B$,[6] Piers' reagent forms "frustrated Lewis pairs"[7] when combined with bulky Lewis bases such as P^tBu_3 or $PMes_3$. Heterolytic cleavage of hydrogen by these systems generates $[R_3PH][(C_6F_5)_2H_2B]$.[8] However, this anion is not stable, and under air- and moisture-free conditions disproportionation can occur to give $[R_3PH][(C_6F_5)_3HB]$ and $[R_3PH][(C_6F_5)H_3B]$, while subsequent release of hydrogen yields dimeric $[H_2B(C_6F_5)]_2$.[8] To the best of our knowledge, this is the only report in the open literature of the base-free monopentafluorophenylborane.

Scheme 1



Hoshi et al. have recently shown that the reagent generated *in situ* from a 1:1 mixture of $(C_6F_5)_3B$ and $H_3B \cdot SMe_2$ was effective at promoting the hydroboration of an alkyne with pinacolborane.[9] The solution phase was characterized by ^{11}B spectroscopy, which indicated the presence of $(C_6F_5)_3B$, $(C_6F_5)_2HB$, and $(C_6F_5)H_2B$ as their dimethyl sulfide adducts.[9] Evidently there is facile exchange between hydride and pentafluorophenyl groups in these boranes, in contrast to the lack of reactivity between tris(pentafluorophenyl)borane and boron trihalides.[10] The observation of a mixture of products is not surprising given the stoichiometry and dimethyl sulfide deficiency in a 1:1 reaction.[11]

The facile nature of the hydride and pentafluorophenyl ligand exchange and the labile nature of the dimethyl sulfide ligand suggested that Hoshi's procedure might be refined to provide an alternative to Piers' syntheses. The dimethyl sulfide adduct of bis(pentafluorophenyl)borane should retain much of the utility of Piers' borane, particularly for hydroboration and the preparation of Lewis basic adducts. Furthermore, providing the appropriate stoichiometry, this approach might be amenable to the preparation of the dimethyl sulfide adduct of the mono(pentafluorophenyl)borane. Herein we report the fast and convenient syntheses of the dimethyl sulfide adducts of mono- and bis(pentafluorophenyl)borane from tris(pentafluorophenyl)borane and the borane−dimethyl sulfide adduct.

Results and Discussion

Treatment of a light petroleum solution containing two equivalents of $(C_6F_5)_3B \cdot OEt_2$ with one equivalent of $H_3B \cdot SMe_2$ resulted in the precipitation of oily droplets on the sides of the reaction vessel. The subsequent addition of an excess of dimethyl sulfide resulted in a portion of the oil

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(7) For recent reviews on "frustrated Lewis pairs", see: (a) Stephan, D. W. *Dalton Trans.* **2009**, 3129. (b) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46.

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(11) The active species for hydroboration is believed to be $[(C_6F_5)_2HB]$, resulting from dissociation of the weakly bound dimethyl sulfide ligand.

Scheme 2

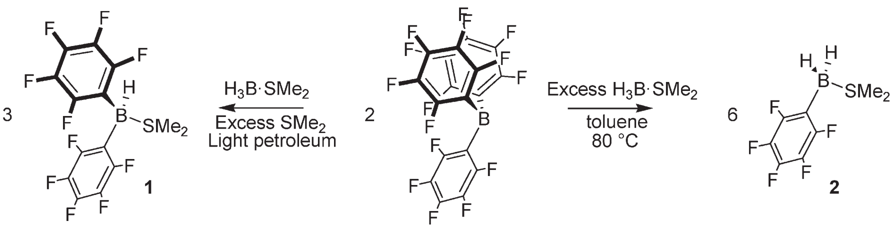

Table 1. Multinuclear NMR Data for Solutions in C_6D_6 at 23 °C

	^{1}H		^{11}B	^{19}F		
	BH	Me		*o*-F	*m*-F	*p*-F
$(C_6F_5)_3B\cdot SMe_2$		0.94	−3.2	−129.6	−162.1	−153.6
1	3.60	1.09	−11.9	−131.5	−162.8	−155.9
2	2.84	1.20	−17.2	−130.4	−163.8	−157.6
$H_3B\cdot SMe_2$	2.11	1.46	−19.4			

dissolving while the remainder was separated by filtration.[12] The desired product proved to be moderately soluble in light petroleum and was purified by recrystallization from light petroleum solution at 5 °C to yield a colorless crystalline solid (**1**) (Scheme 2). Compound **1** was formulated as $(C_6F_5)_2HB\cdot SMe_2$ on the basis of the multinuclear NMR characterization (Table 1). The ^{1}H NMR spectrum consisted of a broad multiplet at $\delta = 3.60$ ppm corresponding to the BH signal and a sharp singlet for the dimethyl sulfide groups in the expected 1:6 ratio. Most significantly, the ^{11}B NMR spectrum consisted of a doublet ($^1J_{BH} = 81$ Hz) at significantly lower frequency than that observed for $(C_6F_5)_3B\cdot SMe_2$[13] but at higher frequency than that found for $H_3B\cdot SMe_2$. These assignments are consistent with those reported by Hoshi et al. The bulk composition of **1** was confirmed by elemental analysis.

The solid-state structure was elucidated by X-ray diffraction techniques (Figure 1), and the molecule was found to be disordered over two resolved orientations.[14] The boron center displays near tetrahedral geometry, with the B−S bond lengths slightly shorter than observed in $(C_6F_5)_3B\cdot SMe_2$.[13b] The B−C bond length is slightly longer than observed in the donor-free dimer.[2]

Treatment of $(C_6F_5)_3B\cdot OEt_2$ with two equivalents of $H_3B\cdot SMe_2$ in light petroleum at room temperature resulted in partial conversion to $(C_6F_5)H_2B\cdot SMe_2$. Intriguingly, under these conditions $H_3B\cdot SMe_2$ and $(C_6F_5)_2HB\cdot SMe_2$ undergo only very slow ligand exchange, in contrast to the rapid reaction between $(C_6F_5)_3B\cdot SMe_2$ and $H_3B\cdot SMe_2$. If a modest excess of $H_3B\cdot SMe_2$ is employed and the reaction is conducted in toluene at 80 °C, complete conversion to $(C_6F_5)H_2B\cdot SMe_2$ (**2**) occurs (Scheme 2). In the presence of an excess of $H_3B\cdot SMe_2$ the addition of further Me_2S is unnecessary. Any residual $H_3B\cdot SMe_2$ or $[BH_3]_2$ was easily removed under reduced pressure. Proton-coupled ^{11}B NMR spectroscopy provides an excellent means with which to monitor the reaction, and the generation of a triplet signal at $\delta = -17.2$ ppm ($^1J_{BH} = 105$ Hz) is indicative of a four-coordinate dihydride (Table 1). The frequency of the ^{11}B NMR signal for **2** is intermediate between that for $H_3B\cdot SMe_2$ and **1**, reflecting the systematic variation in electron density, as hydride ligands are replaced by the more electron-withdrawing pentafluorophenyl group. The ^{1}H NMR consisted of a sharp singlet at $\delta = 1.20$ ppm corresponding to the methyl groups and a broad multiplet at $\delta = 2.84$ ppm for the BH_2. Recrystallization of the crude material from dichloromethane−light petroleum solution yielded the pure compound as a colorless crystalline solid, the composition of which was confirmed by elemental analysis.

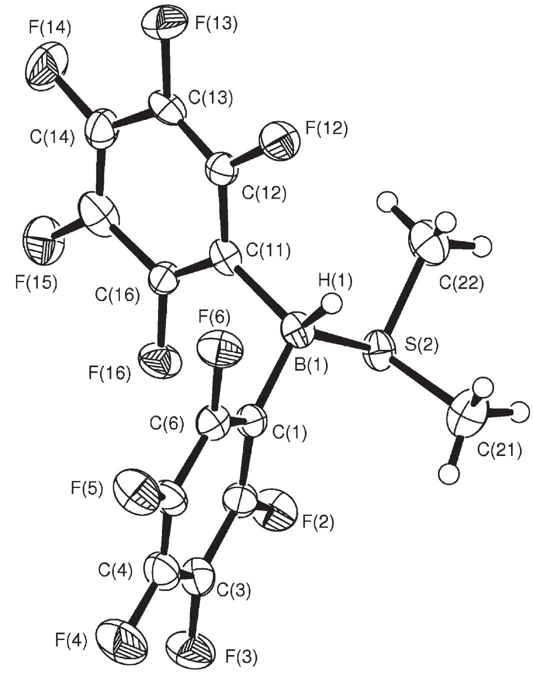

Figure 1. ORTEP of the major component of **1**.[14] Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: B(1)−S(2) 1.963(4), B(1)−C(1) 1.612(6), B(1)−C(11) 1.628(6); C(1)−B(1)−S(2) 112.3(3), C(11)−B(1)−S(2) 105.0(3).

The solid-state structure of **2** was confirmed by X-ray diffraction methods with all hydrogen atoms being located in difference maps and refined freely (Figure 2). The boron adopts a pseudotetrahedral geometry with the B−S bond length only slightly shorter than that observed in $(C_6F_5)_3B\cdot SMe_2$.[13b] The substituents on the boron and sulfur centers adopt a staggered conformation about the B−S bond, and the molecules pack together in pairs through an offset face-to-face

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[12] Comparison of the spectroscopic data for this oily material with an independently prepared reference sample suggests that it is $(C_6F_5)_3B\cdot SMe_2$.

[13] NMR data for $(C_6F_5)_3B\cdot SMe_2$ have previously been reported in $CDCl_3$ and toluene, respectively: (a) Lancaster, S. J.; Hughes, D. L. *Dalton Trans.* **2003**, 1779. (b) Denis, J.; Forintos, H.; Szelke, H.; Toupet, L.; Pham, T.; Madec, P.; Gaumont, A. *Chem. Commun.* **2003**, 54. NMR data in C_6D_6 were collected from a standard sample.

[14] The structure of **1** exhibited significant disorder of the boron and sulfur atoms over two positions, the methyl carbon atoms being common to both components. Full refinement of the C_6F_5 rings of the minor component was not possible since not all atoms could be located in difference maps: the located atoms were refined isotropically.

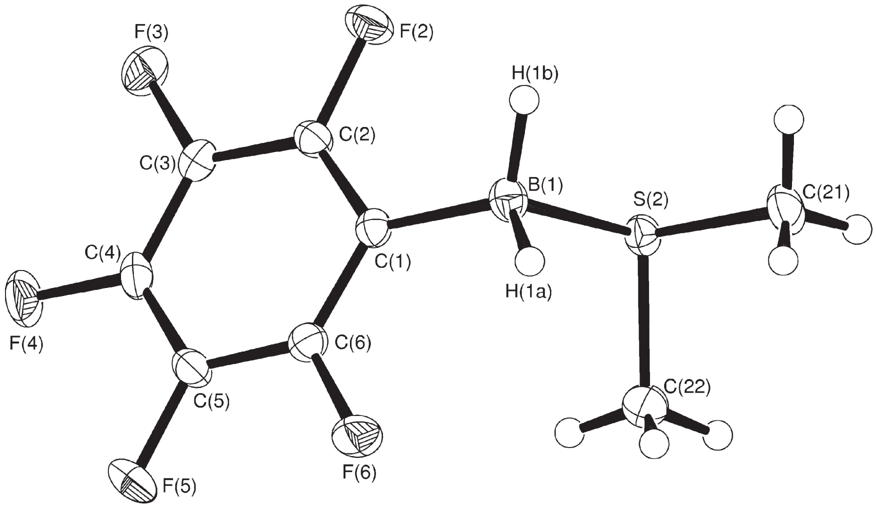

Figure 2. ORTEP of **2**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [deg]: B(1)−S(2) 1.9577(13), B(1)−C(1) 1.604(2); C(1)−B(1)−S(2) 106.66(8).

pentafluorophenyl−pentafluorophenyl interaction about a crystallographic inversion center.

The perfectly atom-efficient synthesis of **1** implied by Scheme 2 is not achieved in practice, at least in part because of the oily precipitate, and the isolated yield is typically just over 50%. An attempt to increase the yield of **1** by conducting the ligand exchange in toluene at 80 °C did not result in an improvement. The preparation of **2** is more efficient, and quantitative conversion was observed by monitoring the reaction mixture by ^{11}B NMR while isolated yields were in excess of 70%. Substituting the diethyl ether adduct for freshly sublimed donor-free tris(pentafluorophenyl)borane does not significantly influence the outcome of these reactions.

Preliminary results indicate that **2** undergoes facile hydroboration with two equivalents of alkenes. Compounds **1** and **2** serve as convenient precursors for Lewis adducts between mono- and bis(pentafluorophenyl)borane and donors such as ammonia.

Conclusion

Treatment of $(C_6F_5)_3B\cdot OEt_2$ with $H_3B\cdot SMe_2$ in the appropriate stoichiometry and where necessary with the addition of Me_2S yields the mono- and bis(pentafluorophenyl)boranes as their dimethyl sulfide adducts $(C_6F_5)_2BH\cdot SMe_2$ (**1**) and $(C_6F_5)H_2B\cdot SMe_2$ (**2**). These compounds can be prepared quickly in good yield from commercially available starting materials.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques in predried glassware. Solvents were dried using an appropriate drying agent and distilled under nitrogen prior to use: dichloromethane (CaH_2), light petroleum (sodium/dyglyme/benzophenone), and toluene (sodium). Dimethyl sulfide was dried over $LiAlH_4$ and distilled prior to use. Samples for NMR analysis were prepared using degassed deuterated solvents dried over activated 4 Å molecular sieves. NMR spectra were obtained using a Bruker Avance DPX300 spectrometer at 23 °C. Chemical shifts are reported in parts per million and referenced to residual solvent resonances (^{1}H, ^{13}C{^{1}H}); ^{19}F is relative to $CFCl_3$; ^{11}B is relative to $F_3B\cdot OEt_2$. Elemental analyses were carried out at the Department of Health and Human Sciences, London Metropolitan University. The synthesis of $(C_6F_5)_3B\cdot OEt_2$ was conducted according to the literature procedure.[15]

Table 2. Crystallographic Data

	1	**2**
chem formula	$C_{14}H_7BF_{10}S$	$C_8H_8BF_5S$
M	408.07	242.01
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a/Å	10.2570(2)	12.1602(6)
b/Å	13.0169(3)	6.0157(3)
c/Å	12.2595(3)	13.4785(7)
β/deg	109.639(2)	99.859(5)
V/Å^3	1541.60(6)	971.42(8)
T/K	140(1)	140(1)
Z	4	4
reflns measd	27 438	18 598
unique reflns, R_{int}	2710, 0.046	2828, 0.041
obsd data	2216	2313
wR_2, R_1 (obsd data)	0.089, 0.048	0.070, 0.027
wR_2, R_1 (all data)	0.096, 0.070	0.072, 0.038
largest diff peak	0.19	0.38

$(C_6F_5)_2HB\cdot SMe_2$ (1). To a solution of $(C_6F_5)_3B\cdot OEt_2$ (6.46 g, 11.0 mmol) in light petroleum (300 mL) was added $H_3B\cdot SMe_2$ (0.52 mL, 5.5 mmol). There was an immediate precipitation of an oil, which aggregated into droplets after stirring for a few minutes. An excess of Me_2S (0.50 mL, 6.8 mmol) was added before the oil was separated by filtration and the filtrate cooled to 0 °C, precipitating an unidentified compound and a small quantity of $(C_6F_5)_2HB\cdot SMe_2$, which was separated by filtration. The filtrate was reduced to approximately half volume and cooled to −25 °C to yield the pure product as a colorless crystalline solid (3.64 g, 54%). X-ray quality crystals were obtained by recrystallization from light petroleum solution at 5 °C. Anal. Calcd (found): C, 41.2 (41.2); H, 1.7 (1.9). ^{1}H NMR (C_6D_6): δ 3.60 (1H, br s, BH), 1.09 (6H, s, CH_3). ^{13}C NMR (C_6D_6): δ 21.8 (CH_3). ^{11}B NMR (C_6D_6): δ −11.9 (1B, d, J = 81 Hz). ^{19}F NMR (C_6D_6): δ −131.5 (4F, d, J_{FF} = 20 Hz, *o*-F), −155.9 (2F, t, J_{FF} = 20 Hz, *p*-F), −162.8 (4F, m, *m*-F).

$(C_6F_5)H_2B\cdot SMe_2$ (2). An excess of $H_3B\cdot SMe_2$ (2.40 mL, 25.3 mmol) was added to a solution of $(C_6F_5)_3B\cdot OEt_2$ (4.36 g, 7.4 mmol) in toluene (60 mL). The solution was heated to 80 °C for 2 h before an aliquot was checked by ^{19}F and ^{11}B NMR to ensure the reaction had gone to completion. The volatiles were removed under reduced pressure to yield a colorless solid.

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Recrystallization from a dichloromethane−light petroleum solution at −25 °C yielded colorless crystals of the pure product (3.95 g, 73%). A further crop was obtained by reducing the solvent volume under reduced pressure and cooling to −25 °C. Anal. Calcd (found): C, 39.7 (39.7); H, 3.3 (2.9). ^{1}H NMR (C_6D_6): δ 2.84 (2H, m, BH_2), 1.20 (6H, s, CH_3). ^{13}C NMR (C_6D_6): δ 22.2 (CH_3). ^{11}B NMR (C_6D_6): δ −17.2 (1B, t, J_{BH} = 105 Hz). ^{19}F NMR (C_6D_6): δ −130.4 (2F, d, J_{FF} = 17 Hz, *o*-F), −157.6 (1F, t, J_{FF} = 20 Hz, *p*-F), −163.8 (2F, m, *m*-F).

X-ray Crystallography. Diffraction data were collected at UEA on an Oxford Diffraction Xcalibur-3 CCD diffractometer and processed using the CrysAlis-CCD and RED programs.[16] The structures were determined by direct method routines in the SHELXS program and refined by full-matrix least-squares methods on F^2 in SHELXL[17] within the WinGX program suite.[18] The results are collated in Table 2. Scattering factors for neutral atoms were taken from literature values.[19] All hydrogen atoms in **1** were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent boron and carbon atoms. All hydrogen atoms in **2** were located in difference maps and refined freely.

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Supporting Information Available: Crystallographic information file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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