Boranes

Conversion of Alkyltrifluoroborates into Alkyldichloroboranes with Tetrachlorosilane in Coordinating Solvents**

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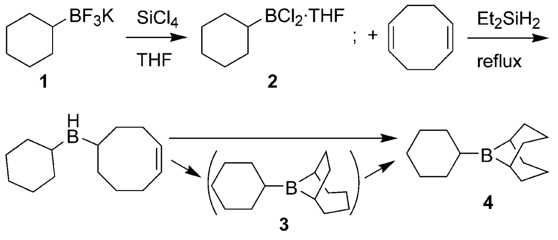
Addition of tetrachlorosilane to organotrifluoroborates, RBF_3K (R = alkyl or aryl), in THF or acetonitrile at 20–25 °C results in immediate evolution of gaseous tetrafluorosilane and formation of the corresponding solvated organodichloroborane, $RBCl_2$. This reaction completes a mild and efficient route from boronic esters to reactive alkyldichloroboranes, which are promising intermediates for asymmetric syntheses.

Previously known chemistry of RBF_3K includes the reaction of $PhBF_3K$ with Me_3SiCl in acetonitrile to form $PhBF_2$.[1] Allylic RBF_3K derivatives react with aldehydes by defluoridation with $BF_3{-}OEt_2$ to give the intermediates RBF_2,[2] or by defluoridation with Bu_4NI/H_2O.[3] Alkylboronic esters of ≈99% stereopurity are available by the reaction of boronic esters of chiral diols with $LiCHCl_2$.[4] Conversion of a stereopure (5-azido-1-phenylbutyl)boronic ester to $N_3(CH_2)_3CH(Ph)BF_3K$ followed by treatment with Me_3SiCl or $SiCl_4$ has been shown to yield 2-phenylpyrrolidine without loss of stereopurity,[5] but the nature of the alkyldihaloborane intermediates was not investigated. The chemistry of RBF_3^- salts has been reviewed in 2003.[6] No previous instance of direct conversion of an RBF_2 to an $RBCl_2$ by means other than B–F/B–Cl exchange has been found in a search of the literature.[7]

The barrier to F/Cl exchange is thermodynamic. Conversion of BF_3 and $SiCl_4$ into BCl_3 and SiF_4 [Eq (1)] is endothermic in the gas phase, $\Delta H^\circ_{298} = +74.014\ \mathrm{kJ\,mol^{-1}}$ or $+6.168\ \mathrm{kJ\,mol^{-1}\,bond^{-1}}$; $\Delta G^\circ_{298} = +64.755\ \mathrm{kJ\,mol^{-1}}$ or $+5.396\ \mathrm{kJ\,mol^{-1}\,bond^{-1}}$.[8]

$$4\,BF_3 + 3\,SiCl_4 \rightarrow 4\,BCl_3 + 3\,SiF_4 \tag{1}$$

The ^{11}B NMR spectra of the products from treatment of potassium (cyclohexyl)trifluoroborate ($CyBF_3K$, **1**; Scheme 1), phenyltrifluoroborate ($PhBF_3K$), or (5-azidopentyl)trifluoroborate $[N_3(CH_2)_5BF_3K]$ with $SiCl_4$ in THF or CH_3CN (Table 1) correspond to solvated $RBCl_2$ and show only minor impurities, including all $SiF_nCl_{(4-n)}$ ($n = 1$–4),[9] in the ^{19}F NMR spectrum. In CH_2Cl_2 with a catalytic amount of [18]crown-6, the reaction stops at $CyBF_2$ or $PhBF_2$, and in Et_2O an unidentified mixture was obtained. The products from Me_3SiCl in all solvents were RBF_2. Commercial $PhBCl_2$ and $PhBF_2$ from $PhBCl_2+NaBF_4$ showed similar NMR spectra. The ^{11}B and ^{19}F chemical shifts of RBF_2 (Table 1) are consistent with tetracoordinate boron in THF but also tricoordinate boron in CH_3CN.[10] The $RBCl_2$ derivatives are tetracoordinate in both solvents. The stronger solvation of $RBCl_2$ evidently favors its formation.



Scheme 1. Conversion of potassium (cyclohexyl)trifluoroborate (**1**) into cyclohexyl-9-BBN (**4**).

Tetrachlorosilane in acetonitrile is the preferred reagent for converting alkyltrifluoroborates and alkyl azides into secondary amines.[5] It is now apparent that the relevant

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Table 1: NMR spectroscopic data for RBF_3K, RBF_2, and $RBCl_2$ in various solvents.

Compound	Solvent	$^{11}B, \delta$	$^{19}F, \delta$	Other
$CyBF_3K$[a]	CD_3CN	5.4	−145.2[b]	$J_{BF} = 63$ Hz
$CyBF_2$	$THF/CDCl_3$	9.6	−149.5	
$CyBF_2$	THF/CD_3CN	9.5	−149.8	
$CyBF_2$	$CH_3CN/CDCl_3$	28	−79.5	
$CyBF_2$	CH_3CN/CD_3CN	33	−79.5	
$CyBCl_2$	$THF/CDCl_3$	15.7	none	
$CyBCl_2$	CH_3CN/CD_3CN	5.7	none	
$PhBF_3K$	CD_3CN	4.0	−141	$J_{BF} = 55$ Hz
$PhBF_2$	$CDCl_3$	24.6	−92	
$PhBF_2$	CD_3CN	11.6	−127.9	
$PhBF_2$	THF/CD_3CN	7.2	−148.6	
$PhBF_2$	$THF/CDCl_3$	7.2	−149.8	
$PhBCl_2$[c]	$CDCl_3$	55	none	
$PhBCl_2$	CD_3CN	3.3	none	
$PhBCl_2$	THF/CD_3CN	12.6	none	
$N_3(CH_2)_5BF_3K$	$CDCl_3$	6.1	−139.2	
$N_3(CH_2)_5BF_2$	$THF/CDCl_3$	9.5	−145.8	
$N_3(CH_2)_5BCl_2$	$THF/CDCl_3$	14.6	none	
$N_3(CH_2)_5BCl_2$	$PhCH_3/CDCl_3$	7.5	none	

[a] Cy = cyclohexyl. [b] Also measured in D_2O, $\delta = -143$ ppm.
[c] Commercial $PhBCl_2$ (Aldrich).

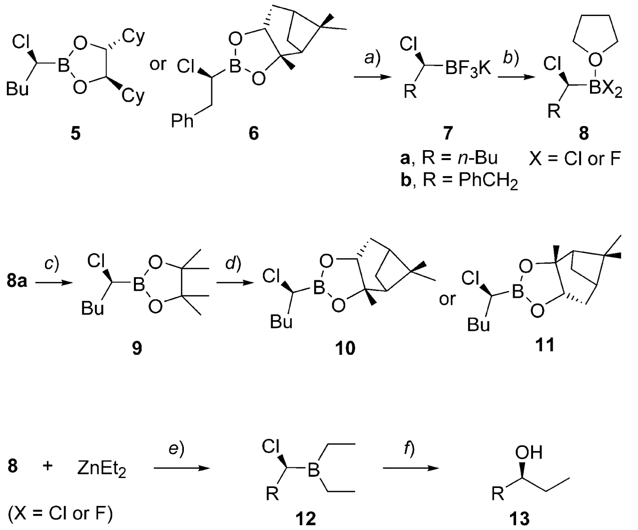
factors are that $RBCl_2$ reacts faster than RBF_2 with alkyl azides and that $RBCl_2$–CH_3CN dissociates more easily than $RBCl_2$–thf. The more weakly solvated primary $RBCl_2$ in diethyl ether react with alkyl azides at 25 °C.[11]

The higher reactivity of $RBCl_2$ compared to RBF_2 is significant in hydroboration chemistry. In noncoordinating solvents, the addition of an alkylsilane to $RBCl_2$ and an alkene results in rapid hydroboration, with clean formation of dialkylchloroborane if the molar ratio of reactants is 1:1:1.[12] However, $CyBF_2$ (≈ 0.3 M in CH_2Cl_2) with Et_2SiH_2 does not hydroborate 1-hexene in 24 h at 20–25 °C. Hydroboration with sterically hindered $RBCl_2$ in the presence of diethyl ether has been reported.[13] Accordingly, we briefly investigated hydroborations of alkenes with Et_2SiH_2 and $CyBF_3K$ (**1**) in THF. Hydroboration is greatly retarded and no pure single product prior to trialkylborane can be produced.

Conversion of $CyBCl_2$ (**2**) and 1,5-cyclooctadiene to cyclohexyl-9-BBN (**4**) in refluxing THF requires ≈ 4 h, or only ≈ 1 h if an equimolar amount of 1-(dimethylamino)-naphthalene is added (Scheme 1). In accord with previous reports,[14] the borabicyclo[4.2.1]nonane isomer **3** (^{11}B NMR: $\delta = 90.1$ ppm) formed nearly as rapidly as the [3.3.1] isomer **4**, (^{11}B NMR: $\delta = 86.3$ ppm), but rearranged into **4**. In contrast to the reaction in the absence of coordinating solvent,[12] 1-hexene could not be converted to CyBClR, R = *n*-hexyl, without generating $CyBR_2$ (^{11}B NMR spectrum: $\delta = 85.3$ ppm).

Reaction of $CyBF_2$ with BCl_3 in CH_2Cl_2 liberates gaseous BF_3 and free $CyBCl_2$, opening the way to the previously described stepwise control of hydroboration,[12] but this chemistry is predictably restricted to $RBCl_2$ without alkoxy or other nucleophilic substituents and has not yet been explored.

Asymmetric (α-chloroalkyl)boronic esters can be converted into (α-chloroalkyl)dichloroboranes without measurable loss of stereopurity. [(*S*)-1-Chloropentyl]boronic ester **5**, prepared from the (butyl)boronic ester and $LiCHCl_2$,[4,15] was converted into the trifluoroborate salt **7a**,[5] then treated with $SiCl_4$ in THF to provide **8a** (Scheme 2). Treatment with methanol and pinacol yielded boronic ester **9** (95 % from **7**). Transesterification of separate portions with the enantiomeric (*S*)- and (*R*)-pinanediol esters produced **10** and **11** in high stereopurity, as shown by their ^{1}H NMR signals in the typically differentiated region,[15] $\delta = 1.15$–1.20 ppm (Figure 1, Scheme 2).



Scheme 2. Reactions of asymmetric alkyldihaloboranes. a) KHF_2.[3] b) For X = Cl, $SiCl_4$ in THF; for X = F, Me_3SiCl/THF. c) 1. MeOH, 0 °C; 2. Pinacol, 25 °C, 1 h, 95 % from **7**. d) (*S*)-Pinanediol yields **10**, (*R*)-pinanediol **11**; filtered through silica. e) Et_2Zn. f) 1. MeOH, NaOMe; 2. H_2O_2, NaOH.

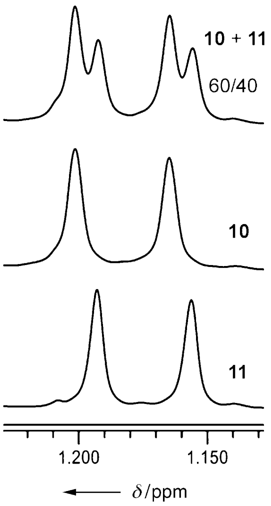


Figure 1. Differentiated ^{1}H NMR signals of (*S*)- and (*R*)-pinanediol (*S*)-1-(chloropentyl)boronates **10** and **11**.

An anticipated future synthetic application of asymmetric (α-chloroalkyl)dihaloboranes such as **8** is for joining two alkyl groups, especially combinations in which neither is available from a Grignard reagent. Connection to boron by hydroboration is not an option because (α-chloroalkyl)hydroboranes undergo rapid self-reduction in THF,[16] but organometallic reagents should be useful. In view of the wide variety of organozinc reagents that have become available from the work of Knochel's group,[17] diethylzinc was chosen for preliminary tests. All four (α-chloroalkyl)dihaloboranes **8** yielded optically active secondary alcohols **13** after treatment with excess diethylzinc followed by sodium methoxide and then alkaline hydrogen peroxide. The enantiomeric purities of **13** have not been verified, but rotations are in the expected range. Yields were satisfactory for **13a**, excellent for the less volatile **13b**. Intermediate **12** from **8a**, $X = F$, was verified by the ^{11}B NMR signal at $\delta = 87.5$ ppm.

Experimental Section

13a: Trifluoroborate **7a** (1.57 g, 7.4 mmol) was stirred for 4 h with $SiCl_4$ (1.2 mL, 14.8 mmol) in THF (20 mL) at 20–25 °C under argon. Most of the excess $SiCl_4$ was removed by concentration under vacuum. The residue of **8a** ($X = Cl$) in THF (20 mL) at 0 °C was treated with $ZnEt_2$ (15 mL, 1 M in hexanes). After 12–16 h MeOH (5 mL) was added at 0 °C. When gas evolution ceased, the mixture was treated with NaOMe (2 g, 37 mmol) at 0 °C, then stirred for 4 h at 20–25 °C. After cooling to 0 °C, aqueous NaOH (5 mL, 3 M) and H_2O_2 (30 %, 5 mL) were added. After 3 h, the mixture was worked up with ether and water and the residue was purified by flash chromatography (10 % ether/pentane) and bulb to bulb distillation of **13a** (0.507 g, 59 %); ^1H NMR ($CDCl_3$): $\delta = 3.52$ (m, 1 H), 1.73 (bs, 1 H), 1.23–1.63 (m, 8 H), 0.94 (t, $J = 7.2$ Hz, 3 H), 0.91(t, $J = 6.9$ Hz, 3 H); ^{13}C NMR ($CDCl_3$): $\delta = 73.3$, 36.6, 30.1, 27.8, 22.8, 14.1, 9.9 ppm; $[\alpha]_D^{22} = +7.9$ ($c = 0.03$ in $CHCl_3$), $[\alpha]_{546}^{22} = +8.9$ ($c = 0.03$ in $CHCl_3$); (lit., $[\alpha]_D = +5.83$ ($CHCl_3$) ("95 % *ee*"));[18] $[\alpha]_D = +6.7$ (neat), $[\alpha]_D = +8.0$ (EtOH), $[\alpha]_D = +8.33$ (Et_2O).[19]

13b: Similar treatment of **7b** (partially epimerized, d.r. 86:14) yielded **13b** (94 %); ^1H NMR ($CDCl_3$): $\delta = 7.18$–7.34 (m, 5 H), 3.73 (m, 1 H), 2.82 (AB, dd, $J = 13.5$, 4.2 Hz, 1 H), 2.63 (AB, dd, $J = 13.5$, 8.4 Hz, 1 H), 1.64 (bs, 1 H), 1.52 (m, 2 H), 0.99 ppm (t, $J = 7.8$ Hz, 3 H); ^{13}C NMR ($CDCl_3$): $\delta = 138.6$, 129.4, 128.5, 126.3, 74.0, 43.5, 29.5, 10.0 ppm; $[\alpha]_D = +15.7$ ($ee < 72$ %, $c = 0.054$ in Et_2O); $[\alpha]_{546} = +20.0$; no literature data available.

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