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Generation of bis(pentafluorophenyl)borane–dimethyl sulfide complex as a solution of hexane and its application to hydroboration of alk-1-yne with pinacolborane

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Abstract—A solution of bis(pentafluorophenyl)borane–dimethyl sulfide complex in hexane was generated by redistribution between tris(pentafluorophenyl)borane and borane–dimethyl sulfide complex. In the resulting solution a stoichiometric hydroboration of alk-1-yne with pinacolborane proceeded well at room temperature to afford (*E*)-alk-1-enylboronic acid pinacol ester in high yield. Bis(pentafluorophenyl)borane–dimethyl sulfide complex served as a mediator for the hydroboration.

Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] is a unique Lewis acid, that is, an air-stable, water-tolerant, thermally robust compound. Due to its distinctive features, it has extensively been used as a Lewis acid catalyst in organic synthesis.[1] In connection with pentafluorophenyl substituted-boron compounds, Piers and co-workers reported that bis(pentafluorophenyl)borane [$HB(C_6F_5)_2$] is an extremely active hydroborating agent towards alkenes and alkynes.[2] Hydroboration with $HB(C_6F_5)_2$ in benzene proceeded at a much faster rate than that with other hydroborating agents. Regarding the preparation of $HB(C_6F_5)_2$, two routes were recommended. One route was a three-step procedure: (1) synthesis of $Me_2Sn(C_6F_5)_2$ by reaction of Me_2SnCl_2 with C_6F_5Li, (2) synthesis of $ClB(C_6F_5)_2$ by transfer of pentafluorophenyl group from $Me_2Sn(C_6F_5)_2$ to BCl_3, (3) synthesis of $HB(C_6F_5)_2$ by treatment of $ClB(C_6F_5)_2$ with $Me_2SiCl(H)$. The other route was that the reaction of $B(C_6F_5)_3$ with Et_3SiH was carried out in benzene at 60 °C for 3 days. The former requires a great deal of time and skill, while the latter is simple but takes much time. Thus, a simple and easy preparation of $HB(C_6F_5)_2$ is desirable for enhancing its utility. Herein we describe a straightforward generation of bis(pentafluorophenyl)borane–dimethyl sulfide complex [$HB(C_6F_5)_2{\cdot}SMe_2$] as a solution in hexane and an application of it as a mediator for hydroboration of alk-1-yne with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane).

Exchange reactions have been reported between $B(C_6F_5)_3$ and other organometallics (main-group metal compounds).[2b,3] We explored the possibility of a preparation of $HB(C_6F_5)_2$ employing redistribution between $B(C_6F_5)_3$ and borane–dimethyl sulfide complex ($BH_3{\cdot}SMe_2$), both of which are commercially available. The redistribution reaction was examined in some solvents, such as hexane, benzene, 1,2-dichloroethane, $CDCl_3$ and DME, using ^{11}B NMR spectroscopy. When using hexane as the solvent, the predominant generation of $HB(C_6F_5)_2$ was observed. Thus, a mixture of $B(C_6F_5)_3$ (0.05 mmol) and $BH_3{\cdot}SMe_2$ (0.05 mmol) in hexane (1 mL) was stirred for 1 h at room temperature to give a clear liquid and a white solid sticking to the glass surface of the reaction flask. The ^{11}B NMR spectroscopy of the clear liquid revealed only a doublet at δ −10.9 ($J = 107$ Hz), indicating that $HB(C_6F_5)_2$ had been formed in hexane (Fig. 1). The signal of $HB(C_6F_5)_2$ was found further upfield than that reported in the literature,[2] probably due to the complexation between $HB(C_6F_5)_2$ and Me_2S. The white solid was dissolved with $CDCl_3$, and then the solution was analyzed by ^{11}B NMR spectroscopy. The spectrum exhibited three

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Keywords: Bis(pentafluorophenyl)borane–dimethyl sulfide complex; Tris(pentafluorophenyl)borane; Borane–dimethyl sulfide complex; Hydroboration; Pinacolborane.

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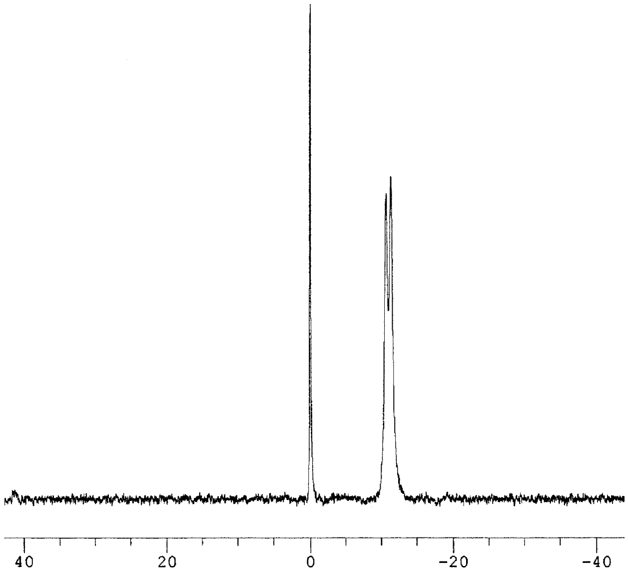


Figure 1. ^{11}B NMR spectrum of the clear liquid after the reaction of $B(C_6F_5)_3$ with $BH_3 \cdot SMe_2$ in hexane (160 MHz; $BF_3 \cdot OEt_2$).

signals: a triplet at δ −8.0 ($J = 127$ Hz), a singlet at δ −2.3 and a doublet at δ 26.2 ($J = 180$ Hz) in a ratio of 1:3:1.5 (Fig. 2). The signal of the triplet was assigned to $H_2B(C_6F_5)$ and the signal of the singlet was in agreement with that of $B(C_6F_5)_3$. It is recognized that dimeric dialkylborane displays a signal in the δ 25–30 region.[4] The signal of the doublet was thus assigned to $HB(C_6F_5)_2$, which was dimeric species in solution. It should be noted that $HB(C_6F_5)_2 \cdot SMe_2$ can be obtained conveniently as a solution in hexane, despite the coexistence of other boranes. We also examined the reaction of $B(C_6F_5)_3$ (0.05 mmol) with an excess amount of $BH_3 \cdot SMe_2$ (more than 0.05 mmol) in order to improve the formation of $HB(C_6F_5)_2 \cdot SMe_2$. The ^{11}B NMR spectroscopy of the reaction mixture (liquid phase) exhibited a triplet at δ −16.2 ($J = 114$ Hz) and a quartet at δ −18.8 ($J = 107$ Hz) as well as a doublet at δ −10.9 ($J = 107$ Hz). The signal of the triplet might be $H_2B(C_6F_5) \cdot SMe_2$ and the signal of the quartet was assigned to $BH_3 \cdot SMe_2$. Consequently, using an excess amount of $BH_3 \cdot SMe_2$ was found to be unfavourable for generating a solution of $HB(C_6F_5)_2 \cdot SMe_2$ in hexane.

With a straightforward generation of $HB(C_6F_5)_2 \cdot SMe_2$ in hand, we then investigated its utilization. Srebnik et al. described that a stoichiometric hydroboration of alkyne with pinacolborane proceeded very slowly without using catalyst.[5] We have previously reported that dicyclohexylborane-mediated hydroboration of alk-1-ynes (**1**) with pinacolborane proceeds under neat conditions at room temperature, affording (*E*)-alk-1-enylboronic acid pinacol esters (**2**) in good to excellent yields.[6] Since $HB(C_6F_5)_2$ hydroborates **1** immediately to produce the corresponding (*E*)-alk-1-enylbis(pentafluorophenyl)borane,[2] $HB(C_6F_5)_2$ may well function as a mediator similar to dicyclohexylborane. We envisioned a mechanism for $HB(C_6F_5)_2 \cdot SMe_2$-mediated hydroboration of **1** with pinacolborane. Thus, hydroboration of **1** with $HB(C_6F_5)_2 \cdot SMe_2$, generated by the redistribution between $B(C_6F_5)_3$ and $BH_3 \cdot SMe_2$, would give (*E*)-alk-1-enylbis(pentafluorophenyl)borane–dimethyl sulfide complex, whose alk-1-enyl group would be replaced with the hydride of pinacolborane to yield product **2** together with regeneration of $HB(C_6F_5)_2 \cdot SMe_2$, which would complete the reaction cycle (Scheme 1). This led us to examine hydroboration of hex-1-yne (**1a**) with pinacolborane in a solution of $HB(C_6F_5)_2 \cdot SMe_2$ in hexane. We were pleased to find that the hydroboration proceeded at room temperature to give (*E*)-hex-1-enylboronic acid pinacol ester (**2a**)[7] in constant yield after stirring for 6 h. Accordingly, we probed the optimum conditions for the reaction of $B(C_6F_5)_3$ with $BH_3 \cdot SMe_2$ in order to obtain product **2a** in high yield. Table 1 shows the results in which the reaction was conducted varying the amounts and rate of $B(C_6F_5)_3$ and $BH_3 \cdot SMe_2$ in hexane at room temperature. As can be

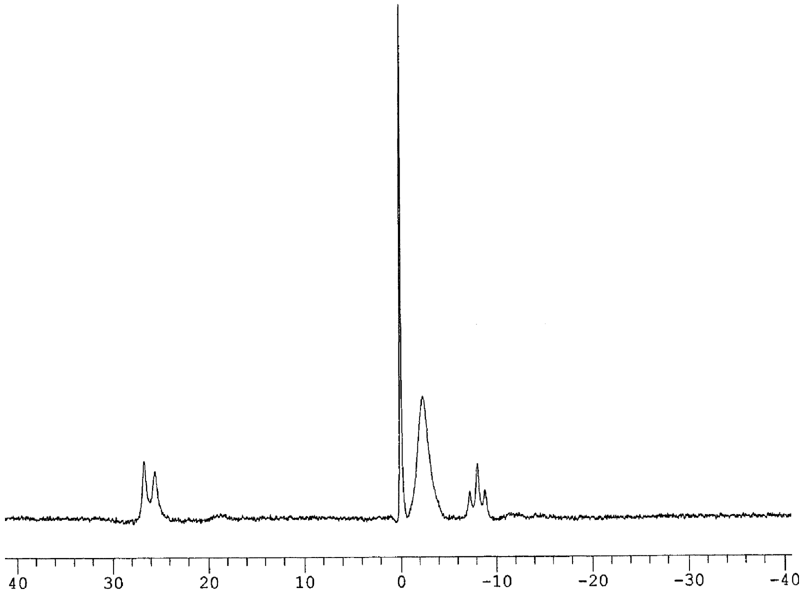
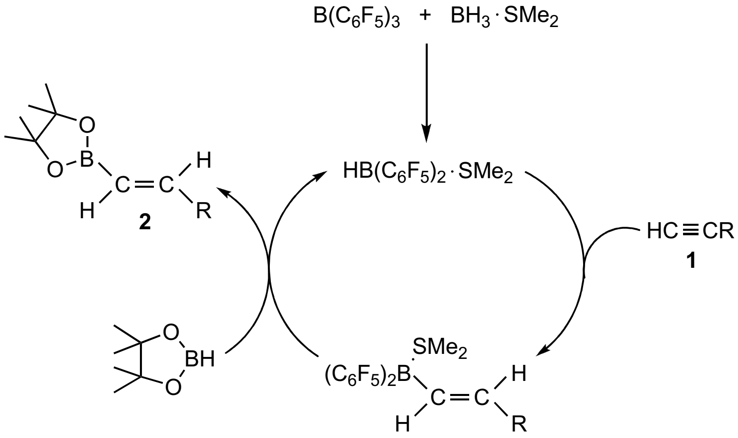
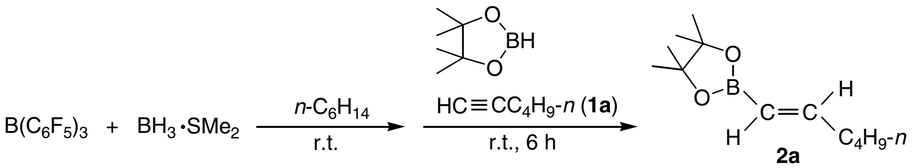


Figure 2. ^{11}B NMR spectrum of the residual white solid after the reaction of $B(C_6F_5)_3$ with $BH_3 \cdot SMe_2$ in hexane (160 MHz; $BF_3 \cdot OEt_2$).



Scheme 1. Reaction mechanism for $HB(C_6F_5)_2 \cdot SMe_2$-mediated hydroboration of alk-1-yne with pinacolborane.

Table 1. Optimization of hydroboration of **1a** with pinacolborane using $HB(C_6F_5)_2 \cdot SMe_2$ generated in situ by redistribution between $B(C_6F_5)_3$ and $BH_3 \cdot SMe_2$[a]



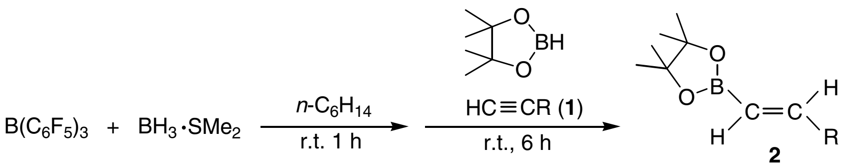
Entry	$B(C_6F_5)_3$ (mol %)	$BH_3 \cdot SMe_2$ (mol %)	React. time[b] (h)	Yield of **2a**[c] (%)
1	0	0	0	Trace
2	1	1	1	47
3	2	1	1	78
4	2	2	1	83
5	2	3	1	84
6	2	4	1	87
7	3	2	1	87
8	3	3	1	92
9	3	3	0.5	86
10	3	4	1	90

[a] Reaction conditions: pinacolborane (1 mmol), **1a** (1 mmol) and n-C_6H_{14} (1 mL).

[b] A period of stirring a mixture of $B(C_6F_5)_3$ and $BH_3 \cdot SMe_2$.

[c] Conversion yield according to GC analysis.

Table 2. Hydroboration of **1** with pinacolborane in the presence of a catalytic amount of $HB(C_6F_5)_2 \cdot SMe_2$ generated in situ by redistribution between $B(C_6F_5)_3$ and $BH_3 \cdot SMe_2$[a]



Entry	R	Yield of **2**[b] (%)
1	*n*-Bu	87
2	*t*-Bu	95
3	$Cl(CH_2)_3$	80
4	Cyclohexenyl	91
5	Ph	83

[a] The reaction was carried out in n-C_6H_{14} (4 mL) using $B(C_6F_5)_3$ (0.12 mmol), $BH_3 \cdot SMe_2$ (0.12 mmol), pinacolborane (4 mmol) and an alk-1-yne (4 mmol).

[b] Isolated yield.

seen from Table 1, using each 3 mol % of $B(C_6F_5)_3$ and $BH_3{\cdot}SMe_2$ and running the redistribution for 1 h gave the best result (92% yield) (entry 8). To support our proposed mechanism, we conducted the hydroboration of **1a** with pinacolborane in the presence of a catalytic amount of (*E*)-hex-1-enylbis(pentafluorophenyl)-borane–dimethyl sulfide complex in place of $HB(C_6F_5)_2{\cdot}SMe_2$.[8] The hydroboration proceeded in the same way as a result, giving product **2a** in a similar yield to that when $HB(C_6F_5)_2{\cdot}SMe_2$ was employed. This fact indicates that $HB(C_6F_5)_2{\cdot}SMe_2$-mediated hydroboration involves the transfer of alk-1-enyl group from boron to boron and the concomitant transfer of hydride.

Hydroboration of several types of **1**, which bear structurally and electronically diverse substituents, with pinacolborane was carried out under the above optimized conditions, and the results are summarized in Table 2. The reactions proceeded smoothly under the optimum conditions for **1a** to provide the corresponding products **2**[9] in high yields.

In conclusion, we have found that a solution of $HB(C_6F_5)_2{\cdot}SMe_2$ in hexane is generated by the redistribution reaction between $B(C_6F_5)_3$ and $BH_3{\cdot}SMe_2$ at room temperature for 1 h. Moreover, it has been demonstrated that a stoichiometric hydroboration of **1** with pinacolborane can be promoted by using a catalytic amount of $HB(C_6F_5)_2{\cdot}SMe_2$ generated in situ to provide the corresponding products **2** in high yields. It is noteworthy that not only dicyclohexylborane[6,10] but also $HB(C_6F_5)_2{\cdot}SMe_2$ is capable of transferring an alk-1-enyl group from boron to boron.

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7. Analytical data for **2a** agreed very closely with those in the literature.[5]
8. After the redistribution reaction between $B(C_6F_5)_3$ (0.04 mmol) and $BH_3{\cdot}SMe_2$ (0.04 mmol) in hexane (1 mL) at room temperature for 1 h, a solution of $HB(C_6F_5)_2{\cdot}SMe_2$ in hexane, thus obtained, was transferred to another reaction flask by syringe under argon. To the stirred solution was added hex-1-yne (0.08 mmol) at 0 °C, and the reaction mixture was stirred for 1 h at room temperature to form a solution of (*E*)-hex-1-enylbis-(pentafluorophenyl)borane–dimethyl sulfide complex (^{11}B NMR: δ 41.1) in hexane. Hex-1-yne (0.92 mmol) and pinacolborane (1.00 mol) were added to the solution at 0 °C, and the mixture was stirred for 6 h at room temperature.
9. Analytical data for **2** were closely in agreement with those in the literature.[5]
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